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The Journal of the Society of Dyers and Colourists

Volume 77 Number 8

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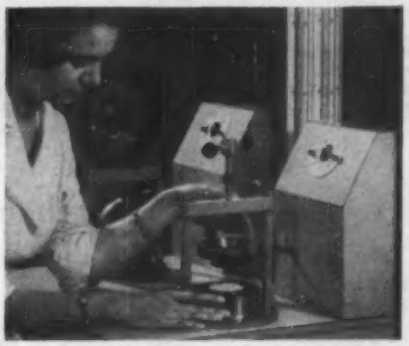

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Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Development of a new Shrink-resist Finish — *A. N. Davidson*

Legal and Practical Problems of Effluent Disposal — *J. H. Harwood*

Chemistry of Thermosetting Resins and Related Compounds — *A. R. Smith*

COMMUNICATIONS

Fibre Surface Contaminants and their Effect in Shrinkproofing — *A. J. Farnworth*

Shrinkproofing Wool with Reducing Agents — *A. J. Farnworth*

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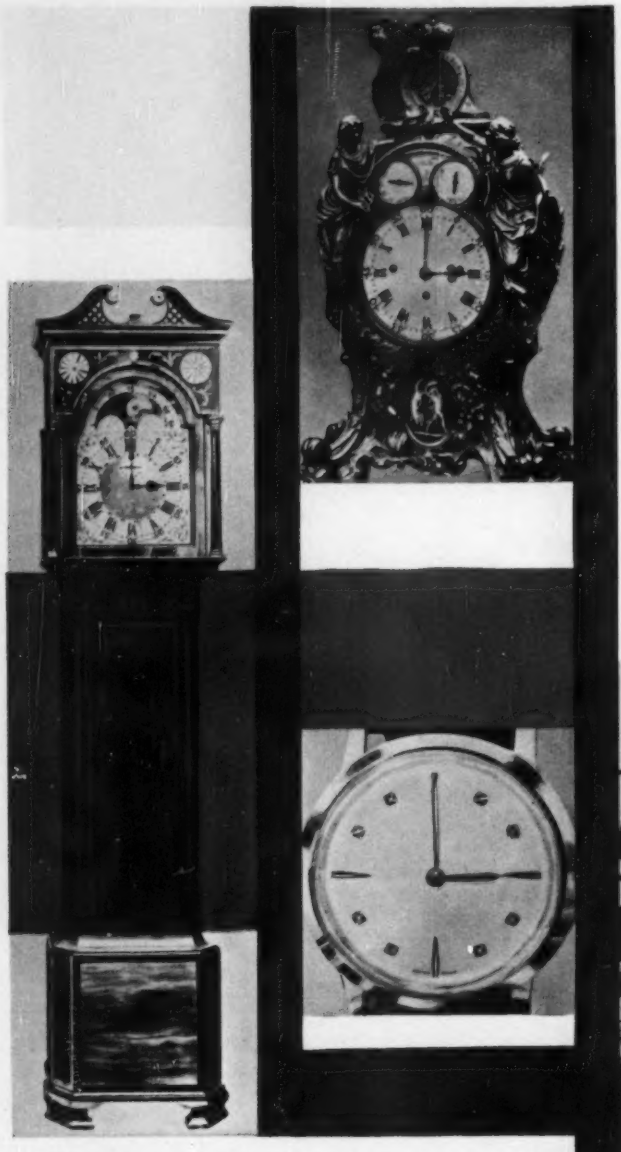

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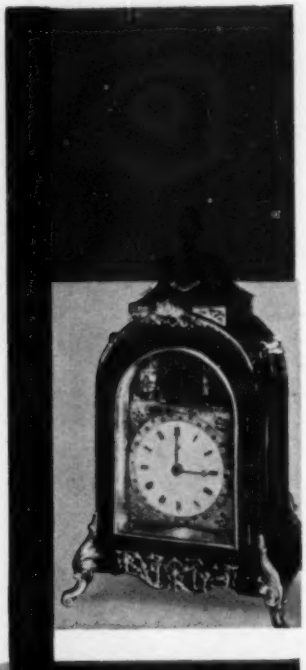

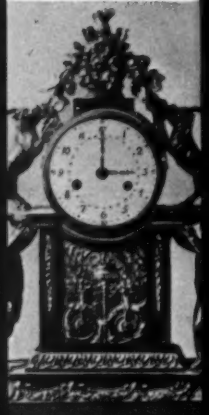

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COMMUNICATIONS

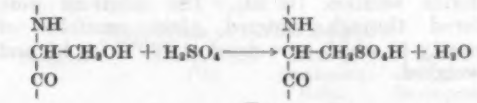
The Effect of Sulphuric Acid on Wool
V— An Investigation of Dyeing Faults caused by Carbonising

R. L. Elliott, R. S. Asquith, and B. J. Jordan

The stability of serine sulphate to hydrolysis with various reagents has been investigated. This ester group is stable to mild hydrolytic treatments both in the free amino acid and in wool protein. Faulty areas in laboratory carbonised and in commercially carbonised wool have been shown to contain a higher concentration of these groups than the surrounding areas, and the groups are apparently responsible for the resistance to acid dyes. Sulphonated derivatives of the aromatic amino acids have not been detected in any fault, and are not therefore responsible for the characteristic unlevel dyeings.

Introduction

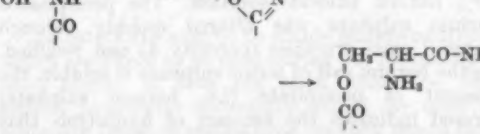
In previous papers [1, 2] it has been shown that the primary reaction of wool with concentrated sulphuric acid is the esterification of the hydroxyl groups of serine and threonine to produce alkyl sulphates—



(I)

Further, it has been established [2] that no reaction occurs between the side-chain amino groups of the wool and sulphuric acid.

Zahn and Hille [3–5], using commercially carbonised wool, have clearly shown that an *O*-peptidyl rearrangement of the serine residues occurs in normal carbonising in a similar manner to that which occurs on treating other proteins [6] with concentrated sulphuric acid, i.e.—



Such a secondary reaction necessarily means that the number of sulphate groups present in the treated wool will decrease as rearrangement proceeds. In support of this, Elliott *et al.* found that the sulphate content decreases on prolonged treatment of wool with concentrated acid [2].

In more recent work [7], the successful isolation of sulphate esters of serine and threonine from carbonised wool confirms that the reactions of wool with cold, concentrated sulphuric acid and with acid under carbonising conditions are very similar, the only major difference being the sulphonation of tyrosine and phenylalanine which occurs on prolonged treatment with concentrated sulphuric acid and possibly in very badly carbonised pieces [8], but not under normal carbonising conditions [9].

The important reactions in carbonising are therefore—

(1) sulphation of the hydroxyl groups of serine and threonine, and

(2) *O*-peptidyl rearrangements of serine residues.

The fact that traces of serine and threonine sulphates can be isolated from wool hydrolysates indicates that they are fairly stable to hydrolysis.

Reaction (1) must, in some way, be responsible for the faults which occur on dyeing carbonised pieces. These faults are characterised by the greater resistance of the wool at the faulty areas to the uptake of acid dyes, which results in uneven dyeing. Elliott *et al.*[1] suggested that resistance was due to the introduction into the wool at the faulty areas of the acidic $CH_2SO_4^-$ side-chains. These negatively charged sites would tend to repel the ionised dye molecule, giving a paler depth, or to completely resist at any place where such groups occur in high concentration. Electrophoresis [7, 10] indicates that these sulphate groups are strongly acidic and could be expected to be negatively charged even at low pH values. The effect would therefore be noticeable over the whole pH range used in dyeing.

In support of this, it is known that when drops of water fall on an acid-treated piece characteristic

light rings occur at the limit of the spread. This is believed to be due to the migration of sulphuric acid from the point where the drop falls to the outer limits of the spread, where the higher concentration then causes a fault.

The present work was carried out to determine if, in fact, higher concentrations than normal of bound sulphate occur in faulty areas.

Experimental

PREPARATION OF WOOL PIECES

The wool flannel used throughout the investigation was unscoured material supplied by Messrs. Kelsall & Kemp. Small pieces used for laboratory carbonising were degreased by Soxhlet-extraction with ether for 24 h and then with alcohol for a similar period. The flannel was next washed in running water for 24 h and allowed to dry at room temperature. Any visible vegetable matter was then removed manually.

The large piece used for commercial carbonising was given a light soap and soda scour before carbonising.

LABORATORY CARBONISING

Pieces of flannel (16 in. × 16 in.) were folded in the manner shown in Fig. 1. The folds were held in position by stitching with Terylene thread at A, B, C, and D. Six folds were made in each piece of material. This type of fold was expected to cause dyeing faults at Y as compared with the normal material at X; these suppositions were proved correct by dyeing tests.

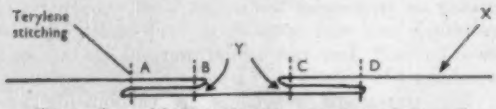


FIG. 1— Type of fold introduced to cause dyeing faults at Y

The folded material was immersed in sulphuric acid of appropriate concentration (2, 5, or 10%), and thoroughly wetted out. Excess of acid was then squeezed out in a laboratory mangle and the material dried in a laboratory oven at 80°C for 30 min, and baked in a second oven at either 111 or 122°C for 15 min. This simulates the predrying and baking stages, respectively, the latter temperature frequently being used in commercial carbonising. (Treatment was never as even, however, as that obtained in a commercial process.) The edges of each piece ($\frac{1}{2}$ in. all round) were removed and the remainder of the cloth divided into three strips, one narrow and two broad, along its length, and the folds released.

Treatment of Strips

The narrow strip was used for detecting the position of faults by dyeing, using the method described by Peel [11]. From the second strip, suitable faulty areas were cut out and pieces of undamaged material of similar size were taken from adjacent parts of the flannel. These pieces were thoroughly washed in running water (for 4 h) to remove as much unbound sulphuric acid as possible and then examined separately for hydrolysable sulphate. The third strip was divided and washed in the same manner as the second and was used for determinations of free sulphuric acid.

COMMERCIAL CARBONISING

Folds, as previously described, were stitched at intervals of 18 in. across the width of a half-piece of wool flannel, which was then carbonised by a normal commercial process*. The carbonised flannel was divided into three equal parts (across the width), the folds were released and the three parts treated as follows—

(1) analysed for sulphate directly after baking,
(2) thoroughly washed in cold water, then analysed,
(3) washed in dilute soda, next in water and then analysed.

All aftertreatments were performed under normal commercial conditions.

Each part was then divided into three strips along its length, as in the laboratory carbonising treatment, and treated in a similar manner, except that no further water washing was given before analyses were made.

ANALYTICAL PROCEDURES

Total Sulphate [12]

Samples (0·5–1 g) of dried wool were refluxed with 20 ml of 6-N HCl for 4 h. The solution was filtered through a small Whatman No. 1 filter paper which was then washed well with water. The solution was made up to volume. Aliquots (10 ml) were withdrawn, diluted to 100 ml, boiled, and the sulphate precipitated with 10% barium chloride solution (10 ml). The solutions were filtered through sintered glass crucibles of porosity 4† which were dried at 120°C for 4 h and reweighed.

Free Sulphuric Acid

The free sulphuric acid content of the wool was determined by the pyridine method of Barritt [13].

Estimation of Sulphate in Hydrolysis of Serine Sulphate

A sample (2 g) of serine sulphate was dissolved in 250 ml of the hydrolysing agent, e.g. 0·1-N HCl, and allowed to stand at constant temperature (50°C). Aliquots (20 ml) were withdrawn and analysed for ionic sulphate by acidifying with 5 ml of 6-N HCl and immediately adding 20 ml of 10% barium chloride solution. The precipitated barium sulphate was filtered quickly through sintered glass crucibles (porosity 4) and weighed. As the barium salt of serine sulphate is soluble, the amount of precipitate (i.e. barium sulphate) formed indicates the amount of hydrolysis that has occurred.

Examination of Faults for Sulphonated Amino Acids

The damaged pieces were examined for sulphonic acid derivatives of tyrosine and phenylalanine as follows.

* By the Calder Carbonising Co., to whom thanks are due.

† *BS* 1752:1952 Sintered disk filters for laboratory use.

The material (0·1 g) was refluxed with 6-N hydrochloric acid for 24 h and the hydrolysate then evaporated to dryness three times with water. The resultant mixture of amino acids was dissolved in borate buffer at pH 8 and separated by low-voltage paper electrophoresis on EEL X118 electrophoresis apparatus on Whatman No. 1 paper. The positions of the acidic amino acids were identified by running a control slip alongside the main electrophoretic run consisting of tyrosine and phenylalanine sulphonic acids, and aspartic and glutamic acids. This was used as a template and fractions were cut from the main run at places where these acids would be expected.

The amino acids of these acidic fractions were extracted from the paper by inserting the rolled paper in a semi-micro condenser and continuously refluxing 5 ml of water over the paper. The solutions were concentrated and applied to two-dimensional chromatograms using butanol–acetic acid–water and phenol–water as solvents. The known sulphonic acid derivatives of tyrosine and phenylalanine were used as controls.

In none of the faults examined were any sulphonated derivatives of the amino acids observed.

Results and Discussion

Preliminary experiments were carried out to determine the stability of the sulphate esters towards various treatments. Synthetic serine sulphate was submitted to hydrolytic treatments and the amount of breakdown estimated. The results of these reactions are summarised in Table I.

TABLE I

Hydrolysis of Serine Sulphate

Reagent	Temperature (°C)	Time of treatment (min)	Serine sulphate decomposed (%)
1% Pyridine solution	30	60	0·60
		180	0·65
		240	0·59
		300	0·61
0·5-N HCl	50	20	1·0
		40	2·3
		80	4·0
		120	6·3
1-N NaAc	50	20	0·5
		40	0·5
		80	0·5
		120	0·7

The esters are seen to be stable under conditions which are likely to be used during the processing of wool fibres. It does not seem, therefore, that simple hydrolytic techniques could be used to eliminate faults in carbonising, as they would have to be so strenuous as to damage the wool. To confirm if the sulphate esters in wool fabric are as stable as those in the model compound, experiments were carried out on fabric which had been heavily damaged with sulphuric acid. It is well-known that if wool fabric is spotted with concentrated sulphuric acid and the acid immediately washed out, the resultant spots are completely resistant to acid dyes. In the present work, wool flannel was dipped in concentrated sulphuric acid and immediately washed with water. This treated wool (completely resistant to acid dyes) was given various washing treatments, and the percentage of bound sulphate and pyridine-extractable sulphate determined. The results of these analyses are shown in Table II.

TABLE II

Sulphate Content of Wool Treated with Conc. H_2SO_4

Reagent*	Temperature	Time of treatment	Total sulphate in wool† (%)	Pyridine-extractable sulphate† (%)
Water (running)	15	2 h	11·26	0·36
Water (large excess)	100	2 h	10·52	0·00
1% Sodium carbonate	20	2 h	10·00	0·00
10% Sodium carbonate	100	5 min	10·34	0·00

* All samples of wool were dipped in 98% sulphuric acid for 1 min and then washed for 2 h in running water prior to the treatment listed.

† After treatment.

Free sulphuric acid, as estimated by pyridine extraction, is relatively easily removed, even by washing in running water for four hours. The sulphate present in the bound form cannot be entirely removed either on boiling with water or by alkaline treatments sufficient to cause visible gelation of the wool (e.g. boiling 10% sodium carbonate), the amount of bound sulphate present in the wool being only slightly reduced by these treatments.

It is interesting to note that the figures for total sulphate are in good agreement with those obtained in previous work [1], i.e. 10·00–11·26%, as compared with 10·65–10·80%. This value is presumably as near the theoretical one of 12·2% for bound sulphate (assuming all hydroxyl groups of serine and threonine have reacted) as can be obtained.

From these results it is obvious that sulphate ester groups in wool are sufficiently stable to resist hydrolysis in normal processing and, therefore, if present in different amounts at various places in the fabric after carbonising, would be responsible for the variability of dye uptake, i.e. faults.

Faults can often be produced by creases in the woollen piece as it passes through the carbonising process. Faulty areas were therefore deliberately induced in wool flannel by creasing (*see* Experimental) and the pleated wool was then submitted to laboratory carbonising, with baking at 122 or 111°C, the initial concentration of carbonising acid being 2, 5, or 10%.

Table III gives the results of determinations of the total sulphate content of the flannel after carbonising at 122°C. In all cases, where a fault occurs the total sulphate content in the faulty region is higher that in the surrounding "normal" parts, despite thorough washing before analysis. Results of the Peel test [11] showed that a definite characteristic fault occurs when the difference between the percentage total sulphate content of

TABLE III

Total Sulphate Content of Laboratory-carbonised Wool, Baked at 122°C

Concentration of acid applied to fabric (% w/v)	Total sulphate (%) in expected faulty area (1)	Total sulphate (%) in adjacent normal piece (2)	Difference in sulphate contents (1)−(2)	Appearance of fault*
2	2·97	2·21	0·76	+
	3·08	2·26	0·82	+
	2·98	2·24	0·74	+
5	3·72	1·90	1·82	++
	3·91	1·87	2·04	++
	3·96	1·95	2·01	++
10	5·86	2·73	3·13	+++
	5·95	2·83	3·12	+++
	5·90	2·77	3·13	+++

* According to Peel test [11], by comparison with adjacent piece
\+ Fault just detectable
++ Fault easily detectable
+++ Strong fault

the "faulty" flannel and that of the "normal" flannel exceeds approx. 0·75%. Again, it can be seen that the greater the initial concentration of sulphuric acid, the greater is the difference between the sulphate contents, and the more intense the fault. When a very low concentration (2%) of sulphuric acid was used, however, test strands of cotton in the material were not sufficiently carbonised to effect removal, and hence reducing the concentration of acid applied could not be used as a palliative for faults.

TABLE IV

Total Sulphate Content of Laboratory-carbonised Wool, Baked at 111°C

Concentration of acid applied to fabric (% w/v)	Total sulphate (%) in expected faulty area (1)	Total sulphate (%) in adjacent normal piece (2)	Difference in sulphate contents (1)−(2)	Appearance of fault*
2	2·41	1·55	0·86	+
	2·36	1·56	0·80	+
	2·36	1·56	0·80	+
5	4·41	1·54	2·87	+++
	4·32	1·51	2·81	+++
	4·40	1·50	2·90	+++
10	5·23	1·88	3·35	+++
	6·25	2·94	3·31	+++
	5·86	2·85	3·01	+++

* According to Peel test [11], by comparison with adjacent piece
\+ Fault just detectable
++ Fault easily detectable
+++ Strong fault

When carbonising was carried out at a lower baking temperature (Table IV) no noticeable improvement occurred, and clear faults were still obtained where high sulphate contents were found.

It has been shown that extraction with pyridine under normal conditions, for the estimation of free sulphuric acid in wool, does not hydrolyse free serine sulphate or serine sulphate bound in the wool. To check that the sulphate estimated was covalently bound, pyridine-extractable sulphuric acid was determined on the carbonised wool. Tables V and VI list the amounts of sulphuric acid extractable by pyridine from both normal and faulty wool. When these amounts are deducted from the total sulphate the discrepancy between faulty and normal pieces remains. It is obvious that the amount of free sulphuric acid extracted is not necessarily diagnostic of a fault.

TABLE V

Estimation of Total Sulphate and Pyridine-extractable Sulphate in Wool Fabric Baked at 122°C

Concentration of acid applied to fabric (% w/v)	Condition of fabric*	Total† sulphate (%) (1)	Pyridine-extractable sulphate (%) (2)	Covalently bound sulphate (%) (1)−(2)
2	+	3·01	2·05	0·96
	normal	2·24	2·00	0·24
5	++	3·86	2·03	1·83
	normal	1·91	1·65	0·26
10	+++	5·90	3·96	1·94
	normal	2·78	2·06	0·72

* According to Peel test [11], by comparison with adjacent piece
\+ Fault just detectable
++ Fault easily detectable
+++ Strong fault
† Mean value from Table III.

TABLE VI

Estimation of Total Sulphate and Pyridine-extractable Sulphate in Wool Fabric Baked at 111°C

Concentration of acid applied to fabric (% w/v)	Condition of fabric*	Total† sulphate (%) (1)	Pyridine-extractable sulphate (%) (2)	Covalently bound sulphate (%) (1)−(2)
2	+	2·38	1·26	1·12
	normal	1·56	1·37	0·19
5	+++	4·38	2·02	2·36
	normal	1·52	1·11	0·41
10	+++	5·78	3·83	1·95
	normal	2·56	1·61	0·95

* According to Peel test [11], by comparison with adjacent piece
\+ Fault just detectable
++ Fault easily detectable
+++ Strong fault
† Mean value from Table IV.

The results, corroborating previous work on the modes of reaction of sulphuric acid with wool, also show that the major factor in carbonising responsible for dyeing faults is the formation at the faulty places of stable alkyl sulphates.

Gaafer and Speakman [14] suggested that faults are caused by the formation of tyrosine sulphonic acids during carbonising. Köpke and Nilssen [8] also found that, on hydrolysis of wool which had suffered severe carbonising damage, traces of unknown amino acids, believed to be tyrosine sulphonic acids, could be detected chromatographically in the wool hydrolysates. Although these acids are formed on treating wool with concentrated sulphuric acid [2], they could not be detected in any of the faults here described and it can be concluded that these acids are formed only when damage is exceptionally severe.

Analyses were next carried out on commercially carbonised wool in which faults had been deliberately introduced, firstly to see if the same effect had occurred and secondly to see if the method of washing had any effects on the faults. The commercially carbonised wool was examined before washing, after washing with water, and after

washing with alkali. It can be seen from Table VII that the wool, after baking, contains variable amounts of sulphate in all parts of the fabric. There is no indication that sulphuric acid is present in excessive amounts in the faulty areas.

TABLE VII

Sulphate Content of Commercially Carbonised Wool before Washing

Total sulphate (%) in expected faulty areas*	Total sulphate (%) in adjacent normal pieces
5·74	6·94
6·09	6·52
7·91	4·89
5·51	5·54

* No tests for actual faults were carried out.

present, whilst after rinsing with sodium acetate solution 1·6% sulphate remained in the wool and 0·6% could not be extracted with pyridine. These figures are similar to those obtained here for normally carbonised wool. In all cases examined the bound sulphate in normally carbonised wool varied between 0·18 and 0·82%. In all faulty areas the content of bound sulphate was much higher, usually between 1·1 and 2·5%.

It can therefore be concluded that faults are caused by higher concentrations of alkyl sulphate bound in the fibre at the faulty areas. The stability of this group to hydrolysis indicates that its removal without damaging the wool will not be easy.

TABLE VIII

Sulphate Content of Commercially Carbonised Wool after Washing with Water

Total sulphate (%)		Pyridine-extractable sulphate (%)		Bound sulphate (%)			
At expected fault (1)	Normal adjacent piece (2)	At expected fault (3)	Normal adjacent piece (4)	At expected fault (1)−(3)	Normal adjacent piece (2)−(4)	Difference in bound sulphate contents	Appearance of fault
3·10	2·90	3·18	2·98	−0·08	−0·08	0·00	Normal
3·11	2·90	3·01	2·92	0·10	−0·02	0·12	Normal
3·45	2·11	2·51	2·38	0·94	−0·27	1·21	+

TABLE IX

Sulphate Content of Commercially Carbonised Wool after Washing to pH 8 with Soap/Soda

Total sulphate (%)		Pyridine-extractable sulphate (%)		Bound sulphate (%)			
At expected fault (1)	Normal adjacent piece (2)	At expected fault (3)	Normal adjacent piece (4)	At expected fault (1)−(3)	Normal adjacent piece (2)−(4)	Difference in bound sulphate contents	Appearance of fault
1·51	0·75	0·00	0·00	1·51	0·75	0·76	+
1·51	0·67	0·00	0·00	1·51	0·67	0·84	+
1·38	0·60	0·00	0·00	1·38	0·60	0·78	+

Unfortunately, faults (as indicated by the Peel test) were not always obtained as expected. It can be seen that in the water-washed wool (Table VIII) only one minor fault actually occurred in the pieces examined and only in this case was there a difference in sulphate content between the normal and faulty parts. It cannot be concluded that this method of washing off tends to decrease faults, however, as in other treatments faults were not always successfully produced.

On the piece washed with alkali, of the eleven faulty places stitched into the cloth, only three showed faults on dyeing, and only these were examined (Table IX). The amount of free sulphuric acid is nil, as indicated by pyridine extraction, so that the alkaline wash had neutralised the free acid. Again the sulphate content at a fault is in excess of that in the normally carbonised wool. It is interesting to note that in normal carbonising, in which presumably no faults were examined, Zahn[4] found that after carbonising and before washing 7·6% sulphate was

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Setting of Animal Fibres in Solutions of Thiourea Dioxide

L. S. BAJPAI and C. S. WHEWELL

Data are given on the setting of wool and human hair in solutions of thiourea dioxide under various conditions. The effectiveness of thiourea dioxide is probably associated with the ability of this reagent to reduce –S–S– bonds in the fibre, for fibres in which –S–S– bonds are converted into more stable –C–S–C– linkages do not take a set. Deaminated fibres take a set in thiourea dioxide solution but not in water.

Introduction

Since compounds such as sodium bisulphite, ammonium thioglycollate, and tetrakis(hydroxymethyl)phosphonium chloride facilitate the setting of animal fibres, it would be expected that other reducing agents would behave in a similar manner. The present paper is an account of an investigation of the setting of wool and hair in solutions of thiourea dioxide under various conditions. Although thiourea dioxide is a well-established reducing agent for vat dyes, little attention has been given to its use as a setting agent. It has, however, been mentioned in a patent [1].

Experimental

MATERIALS

Lincoln wool and Chinese human hair purified by conventional methods were used. Chemically modified wool and hair were prepared as described by Bajpai, Whewell, and Woodhouse [2].

REAGENTS

Thiourea dioxide was used in the form of Manofast (Hardman & Holden Ltd.). Other reagents were of analytical reagent quality.

METHODS

Fibres were mounted in setting frames and stretched by 40% in water, then treated for different times under various conditions in solutions of thiourea dioxide or in water. They were removed from the reagent, rinsed in water, and boiled freely in water for one hour. The taut length of each fibre was then measured and the set or supercontraction calculated as a percentage of the original length of the fibre.

Results and Discussion

Values for the set or supercontraction obtained on untreated and chemically modified keratin fibres under various conditions are given in the following tables.

TABLE I

Setting Wool and Human Hair in Boiling Thiourea Dioxide Solutions (pH 5·0) and in Water

Time of setting (min)	% Set*				
	Wool fibres			Human hair	
	in thiourea dioxide		in water	in thiourea dioxide	in water
	0·1%	2·0%		2·0%	
2	−12·4	− 3·6	−27·9	7·5	− 7·9
5	5·8	6·7	−23·2	19·5	−12·0
15	22·7	27·2	− 9·1	24·6	− 6·5
30	23·9	30·0	− 6·3	28·9	− 2·2
60	29·8	30·8	8·4	27·0	5·6
120	32·4	30·5	14·9	27·5	14·5

* Supercontraction is indicated by the minus sign.

TABLE II

Effect of Concentration on Setting of Wool in Boiling Solutions (pH 5·0) of Thiourea Dioxide

Concentration of thiourea dioxide %	% Set* after treatment for 2 min	% Set* after treatment for 120 min
0	−27·9	14·9
0·1	−12·4	32·4
0·2	− 7·7	31·7
0·5	3·0	31·9
1·0	—	30·9
2·0	− 3·6	30·5

* Supercontraction is indicated by the minus sign.

TABLE III

Effect of Temperature on Setting of Wool in 2% Thiourea Dioxide Solution and in Water

Temperature of setting (°C)	% Set* after setting time of 120 min	
	in thiourea dioxide	in water
40	− 6·6	0·3
50	8·8	1·5
60	22·8	− 6·5
70	27·6	−15·0
80	32·9	−15·4
100	30·5	14·9

* Supercontraction is indicated by the minus sign.

TABLE IV

Setting of Chemically Modified Human Hair in Boiling 2% Thiourea Dioxide Solution (pH 5·0) and in Water

Type of fibre	% Set* after setting for 2 min		% Set* after setting for 120 min	
	in thiourea dioxide	in water	in thiourea dioxide	in water
Purified human hair	7·5	—	27·5	—
Deaminated [1] human hair	0·8	−1·0	14·5	−1·1
Human hair treated with 0·65% KCN solution	−1·8	−1·3	− 6·6	−3·8

* Supercontraction is indicated by the minus sign.

It can be seen from the above tables that solutions of thiourea dioxide are much more effective setting agents than water. For example, after being boiled for 15 min in 2% thiourea dioxide, wool fibres take up 27·2% set, whereas they supercontract after being treated in water for the same time. The concentration of the thiourea dioxide solution is important, but if setting is carried out at the boil no advantage is gained by increasing the concentration above 0·1%. Treatment for 15 min in 0·1% thiourea dioxide induces 22·7% set, whereas setting in water for 120 min induces a set of only 14·9%. As would be expected, the setting power of the solution depends on temperature, and a considerable amount of set can

be realised by treatment at 60°C. The higher the temperature, the greater is the set obtained, but little is gained by setting at temperatures above 80°C.

The effectiveness of thiourea dioxide is probably connected with the ability of this reagent to reduce the –S–S– bonds in the fibre by the following sequence of reactions—

$$NH_2{\cdot}C(:SO_2){\cdot}NH_2 \xrightarrow[H_2O]{\text{heat}} NH{:}C(SO_2H){\cdot}NH_2 \xrightarrow{H_2O}$$

$$H_2SO_2 + NH_2{\cdot}CO{\cdot}NH_2$$

$$H_2SO_2 + R{\cdot}S{\cdot}S{\cdot}R \longrightarrow 2RSH + SO_2$$

$$SO_2 + R{\cdot}S{\cdot}S{\cdot}R + H_2O \longrightarrow R{\cdot}S{\cdot}SO_2H + HSR$$

The data given in Table IV clearly show that fibres in which the –S–S– bonds have been converted into the more stable –C–S–C– bonds do not take a set in thiourea dioxide solutions or in water. Deaminated fibres, on the other hand, take a set in thiourea dioxide solutions but not in water.

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A Study of the Chemistry of Carrotting Processes
I—The Effect of Nitric Acid on Rabbit Fur

E. A. ROBINSON and JANICE ROBINSON

The chemical reactions which occur when rabbit fur is treated with dilute nitric acid, a constituent of both mercuric and many non-mercuric carrotting solutions, are investigated under controlled laboratory conditions which are somewhat similar to those used in carrotting processes. The mono-nitration of tyrosine side-chains occurs when certain critical conditions of temperature and reagent concentration are exceeded. Cystine cross-linkages are not affected under the same conditions. There is evidence that the introduction of a nitro group into the tyrosine side-chain may weaken adjacent peptide bonds towards both hydrolysis and oxidation.

Introduction

The felting properties of animal fur are enhanced by applying a solution of mercuric nitrate in dilute nitric acid (mercuric carrotting), or a mixture of dilute aqueous hydrogen peroxide and nitric acid (non-mercuric carrotting), to the tips of the fibres, and then drying at a moderate temperature (40–80°C). Mercuric-carrotted skins are usually allowed to lie overnight at room temperature, after which they are stoved in pairs with the fur innermost. Skins treated with non-mercuric carrotting solutions (which may contain various reagents in addition to hydrogen peroxide and nitric acid) are normally stoved within one hour of the application of the solution and the skins are dried singly with the fur exposed. The process of mercuric carrotting has remained essentially unchanged since it was first used about 400 years ago. The more recent non-mercuric processes can promote a good rate of felting but only by causing considerably more degradation of the fibre tips than is normally produced by the mercuric process.

Suggestions have been put forward to account for the change in the felting characteristics brought about by carrotting processes [1–3], and work has been done on the chemical reactions which occur when animal fur is treated with the reagents present in carrotting solutions [4–6]. In the present series of papers we have confined our investigations to these reactions. As nitric acid is a major component of mercuric carrotting solutions, and of nearly all the commercially available non-mercuric carrotting solutions, we studied first the reactions which occur between this reagent and rabbit fur (the raw material most commonly used for fur-felt manufacture).

The production of a yellow colour (xanthoproteic acid) by the action of nitric acid on proteins has long been used as a qualitative test for proteins. This colour is also formed when tyrosine is treated with nitric acid and, in fact, only proteins which contain tyrosine give a positive xanthoproteic reaction. Much of the early work on this reaction was carried out on silk fibroin, which is rich in tyrosine, and a number of products were identified, e.g. picric acid [7], *p*-nitrobenzoic acid (from globin) [8], oxalic acid and nitrotyrosine [9]. Johnson and Kohmann [10] showed that 3-nitrotyrosine could be obtained by the direct nitration of tyrosine under carefully controlled conditions; the preparation of 3,5-dinitrotyrosine requires quite different nitrating conditions. They also isolated 3-nitrotyrosine from the hydrolysis products of silk that had been treated with nitric acid, but concluded that the tyrosine side-chain in silk does not yield 3,5-dinitrotyrosine under the conditions used (3·65-M nitric acid at room temperature).

Recently, Zahn and Fritze [11] have made a detailed investigation of the action of 1·4-M nitric acid on tyrosine at 70°C. They propose a complex reaction scheme which leads to a number of solid and gaseous products; the most important intermediate formed under these conditions is 3,5-dinitro-4-hydroxyphenyl-lactic acid, which reacts further over a long period to yield several aromatic nitro compounds and oxalic acid. Zahn and Kohler [12] found that all the tyrosine in wool is nitrated by 1-M nitric acid at 70°C in 24 h.

Experimental

PREPARATION OF SAMPLES

Raw Fur

Large mid-winter rabbit skins (grey tame—Petit Bon) were carefully selected, pulled (to remove the guard hairs) and cut (to remove the fur from the pelt). A portion of the centre back of each fleece (i.e. the cut fur) was extracted with ether and the solubility in alkali[13] determined. Only those centre backs with an alkali solubility of less than 6% were used. This precaution was necessary because the alkali solubility of ether-extracted fur from single skins has occasionally been found to be as high as 18%, presumably because of previous bacterial degradation. Forty such centre backs were mixed together and passed through an eight-section blowing machine (to remove the remaining guard hairs and produce a homogeneous blend) and this batch of blown fur was used for all tests reported in this series of papers. Small portions (6 g) of this fur were extracted with ether for 6 h in a Soxhlet apparatus and the ether was then evaporated off. The fur was next dried *in vacuo*, and the batch stored in this condition. Portions (1 g) were withdrawn as required and, after being wetted thoroughly, were packed into glass tubes (90 × 15 mm) through each of which were passed 2 l. of distilled water at the rate of approximately one drop per second. The sample was filtered under suction, dried for 1½ h in a current of air which had been dried by bubbling through concentrated sulphuric acid in a special apparatus fitted with a spray trap, and then dried *in vacuo* over sulphuric acid.

Nitrated Fur

Samples of fur (1 g), prepared by the method described above, were separately treated with nitric acid (*d*, 1·5; 0·4 ml) in glacial acetic acid (20 ml) for 6 h at 20°C. The fur was filtered off and washed successively with acetic acid and ethanol, and then washed with distilled water and dried as above. This treatment resulted in the conversion of 91% of the tyrosine to 3-nitrotyrosine, while at the same time the alkali solubility increased from 4·9% (for fur treated with glacial acetic acid only) to 20·5–21·5%.

TREATMENT OF SAMPLES

A liquor:fur ratio of 5:1 was used throughout for the following reasons—

(*a*) The amount of solution applied to skins in the carrotting process is usually about 25–35% of their weight. The yield of fur is approximately 35% of the weight of the carrotted skins, but only the tips of the fur fibres are treated with carrotting solution (about 25% of the fibre length). As the diameter of the tip end of a rabbit fur fibre is rather less than that of the stem, the liquor applied in practice is therefore between 4 and 5 times the weight of the treated portion of the fur.

(*b*) Under these conditions the change in the concentration of reactants in solution may be calculated from relatively large differences in titre.

Dilute nitric acid (10 ml) was added to purified fur (2 g) in a 2-oz wide-necked stoppered bottle. The fur was squeezed repeatedly with a flat-ended glass rod until it was wetted uniformly. The bottles were immersed in a water-bath at the stated temperature for 20 h. The mixture was filtered under suction through a sintered glass crucible and the wet fur was weighed immediately; the filtrate and the crucible washings were diluted to 100 ml and suitable aliquots were titrated with standard sodium hydroxide. The wet fur was divided into two equal portions, each of which was washed in a glass column with at least 2 l. of water, until the pH of the eluate was about 6, and then dried as described previously. One of the dried samples (about 1 g) was used for determinations of the alkali solubility and the other for the estimation of cystine and tyrosine. The combined weights of these two samples showed the loss in weight due to the nitric acid treatment. All results are corrected to the original weight of fur. (Although this correction is very small in these tests, it is necessary in later tests in which the gain in weight due to uptake of mercury is appreciable.) The same procedure was followed for those tests in which the fur was treated with dilute sulphuric acid.

Determination of Cystine

The method used for the determination of cystine was developed for this investigation[14]. Erratic results for the cystine content of furs which had been treated with nitric acid were found to be due to residual traces of nitric acid; this caused some of the cystine to be destroyed during hydrolysis with 5·6-M hydrochloric acid for 6 h under reflux (Table I).

TABLE I

Effect of Presence of Nitric Acid during Hydrolysis of Fur

Nitric acid (mmole/g of fur)	Cystine (%)	Tyrosine (%)
nil	12·8	3·17
0·23	11·0	2·94
0·45	10·1	2·91
0·70	9·7	2·63
0·90	9·2	2·36

Very thorough washing of treated furs (e.g. by the procedure described under "Preparation of Samples") is necessary to avoid this source of error.

Determination of Tyrosine

One method for the determination of tyrosine depends on the formation of a red colour with 1-nitroso-2-naphthol[15]. The technique required some modification. The reagent blank was found to be variable, but unchanged reagent can be removed by extraction with benzene. The coloured aqueous solution, after twice extracting with benzene, was clarified by passing it through dry filter paper. When this procedure is adopted, the maximum colour development occurs after heating for 3 min in a vigorously boiling water-bath, instead of after 2 min as in the original method. The presence of 3-nitrotyrosine does not interfere with this determination. Traces of residual nitric acid in the fur also affect the determination of tyrosine (Table I).

Determination of 3-Nitrotyrosine

The yellow colour of an aqueous solution of 3-nitrotyrosine is changed to an intense orange by the addition of alkali, a reaction which is typical of *o*-nitrophenols. As the colour of the hydrolysate of an untreated fur, or of a fur treated with reagents other than nitric or nitrous acid, is not intensified by making the solution alkaline, this reaction was used for the determination of 3-nitrotyrosine. A suitable aliquot of the filtered hydrolysate was neutralised and sodium hydroxide was added until the concentration of alkali was 0·1 N. The solution was diluted to a suitable volume with 0·1-N sodium hydroxide. The colour was measured, using an Ilford filter No. 622, against a blank which was prepared by diluting the hydrolysate to the same extent with water. The calibration curve, which was prepared by using pure 3-nitrotyrosine, showed that Beer's Law is followed up to a concentration of 20 mg/l.

Determination of Tryptophan

Tryptophan was determined by the method of Veldsman [16].

Results

EFFECT OF NITRIC ACID ON CYSTINE IN RABBIT FUR

Cystine in fur is not attacked by nitric acid under the conditions used here (Table II), although the alkali solubility increased to as much as 70% in some tests. An investigation of the reaction between nitric acid and wool led to a similar conclusion [12]. The previously reported reduction in the cystine content of rabbit fur caused by treatment with nitric acid and sodium sulphate [4] might be due to inadequate washing of the fur before hydrolysis.

Other tests were carried out in which half-skins were brushed with dilute nitric acid and stoved under the conditions normally used for carrotted skins. The tips of the fibres were intensely yellow after stoving and the alkali solubility of the blown fur was 31%. Tests on this fur and on the fur from the untreated halves of the skins showed that the treatment had not caused any significant decrease in the cystine content.

TABLE II

Treatment of Fur with Nitric Acid at various Temperatures

Test	Temperature (°C)	$[HNO_3]_0$	Cystine (%)	Tyrosine (%)	Tryptophan (%)
Untreated	—	—	12·8	3·17	0·77
1	20	1·095	12·6	3·14	—
2		2·12	12·5	3·21	—
3		2·635	12·9	2·19	—
4		3·12	12·8	0·87	—
5		4·015	12·8	0·53	—
6		5·225	12·4	0·34	—
7	30	1·04	12·5	3·12	—
8		1·645	12·6	1·90	—
9		2·005	12·8	0·62	—
10		2·225	13·0	0·41	—
11		2·635	12·8	0·37	—
12		3·06	12·7	0·28	—
13		3·865	12·7	0·22	—
14	40	0·27	12·7	3·17	—
15		0·54	12·6	3·25	—
16		0·805	13·0	3·27	0·79
17		1·06	13·1	3·23	—
18		1·075	12·6	3·25	0·81
19		1·325	12·9	3·23	<0·02
20		1·395	12·8	0·84	—
21		1·42	13·0	0·38	<0·02
22		1·425	13·0	0·39	—
23		1·49	12·4	0·38	—
24		1·56	12·7	0·32	—
25		1·635	12·9	0·28	<0·02

EFFECT OF NITRIC ACID ON TYROSINE IN RABBIT FUR

All treated furs with a reduced tyrosine content were yellow. The acid hydrolysates of the yellow furs which were treated at 40°C (Tests 20–25) were examined by means of ascending paper chromatography. For the solvent system isobutanol : 2-M acetic acid = 100 : 9, these hydrolysates gave only one yellow spot (R_f = 0·18) which developed a strong orange colour in ammonia vapour. The position of this spot was identical with that of 3-nitrotyrosine (prepared by the method of Johnson and Kohmann [10], m.p. 232°C (decomp.)) which was run at the same time. Other coloured spots, corresponding with the decomposition products found by Zahn and Fritze [11], and including 3,5-dinitrotyrosine, were absent from these chromatograms. These hydrolysates were also examined by two-dimensional ascending paper chromatography using the solvent systems [17] ethanol : butanol : water : propionic acid = 10 : 10 : 5 : 2 and butanol : acetone : water : dicyclohexylamine = 10 : 10 : 5 : 2. After development with ninhydrin these chromatograms were the same as those given by the hydrolysates of untreated fur, except that tryptophan was absent and tyrosine was replaced by 3-nitrotyrosine; the position of this last compound was identical with that of tyrosine, but the colour developed was slate grey instead of the grey-brown which tyrosine forms on development with ninhydrin in presence of dicyclohexylamine.

TABLE III

Conversion of Tyrosine in Fur to 3-Nitrotyrosine by Nitric Acid

Test	Temperature (°C)	Tyrosine reacted (mmole/100 g fur)	3-Nitrotyrosine (mmole/100 g fur)
3	20	5·4	5·8
4		12·7	12·5
5		14·6	14·3
6		15·6	16·0
8	30	7·0	5·6
9		14·1	12·5
10		15·2	13·2
11		15·5	14·4
12		16·0	15·3
13		16·3	16·8
20	40	13·7	14·2
21		15·8	14·8
22		15·7	14·5
23		15·8	15·0
24		16·1	15·4
25		16·3	15·9

As the yellow colour of the hydrolysates appeared to be due to 3-nitrotyrosine exclusively, it was possible to determine the concentration of this compound by measuring the increase in intensity of the colour produced on making the solution alkaline. These measurements show that nearly all of the tyrosine which had reacted was present as 3-nitrotyrosine (Table III). A small amount of 3-nitrotyrosine was also present in the nitric acid filtrates, but as this was always less than 2% of that present in the hydrolysates it does not significantly affect the results in Table III.

Discussion

The results in Table II show that tyrosine side-chains are attacked only when the concentration of nitric acid is sufficiently high; this minimum concentration for reaction decreases sharply with increase in temperature. A plot of alkali solubility against the initial concentration of nitric acid consists of two linear portions, the intersection of which indicates the point at which the fur first takes on a yellow appearance at each of the three temperatures (Fig. 1).

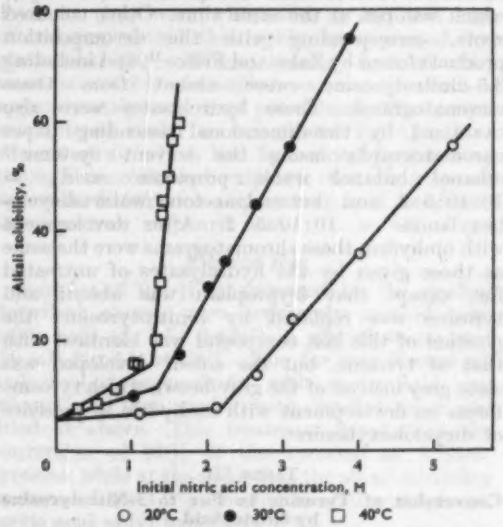

FIG. 1—Effect of initial nitric acid concentration on alkali solubility

Thus the nitration of tyrosine side-chains coincides with the sudden increase in alkali solubility. Two possible explanations of this observation were considered—

(*a*) The introduction of a nitro group *ortho* to the phenolic hydroxyl group in a tyrosine side-chain might so increase the electron demand of the side-chain as to cause the peptide bond adjacent to the tyrosine to become more susceptible to hydrolysis. A similar effect has been observed when cystine cross-links are oxidised to cysteic acid side-chains (which carry the highly electrophilic sulphonic acid group); cysteic acid peptides are readily hydrolysed under mild conditions at the peptide bond adjacent to the cysteic acid [18].

(*b*) At a sufficiently high concentration of nitric acid, peptide bonds may be oxidised. The formation of some nitrous acid might be expected during such a reaction and this would catalyse the nitration of the phenolic side-chain (as it does with phenols in solution [19]). In this case the nitration of tyrosine would be a secondary reaction which of itself should not greatly influence the solubility of the treated fibres in alkali, except in so far as explanation (*a*) applies.

The first explanation was tested experimentally by nitrating fur in glacial acetic acid (see p. 352); hydrolysis of peptide bonds occurs to a lesser extent under these conditions, as is shown by the smaller change in alkali solubility and in acid-combining power (Table IV). In fact, the extent of the hydrolysis which occurs during treatment of fur with aqueous nitric acid is greater than the acid-combining power indicates because some deamination also takes place (see later).

TABLE IV

Treatment of Fur with Nitric Acid in Aqueous and Non-aqueous Solutions

Nitrating medium	Temperature (°C)	Tyrosine nitrated (%)	Alkali solubility (%)	Acid-combining power (mmole/100 g fur)
Untreated	—	nil	5·8	80
1·6-M HNO_3 in water	40	91	59·6	91
0·5-M HNO_3 in glacial acetic acid	20	91	20·5	78

Fur treated in this way was subjected to the action of dilute sulphuric acid (i.e. a non-oxidising acid) at 40°C; the results of these tests are plotted in Fig. 2 (curve C). Although the slope of this curve is steeper than that for the sulphuric acid treatment of raw fur (curve A), it is not steep enough to compare with that part of curve B (nitric acid and raw fur) after the nitration of tyrosine has commenced. Therefore, the first explanation appears to provide only part of the reason for the sharp increase in alkali solubility.

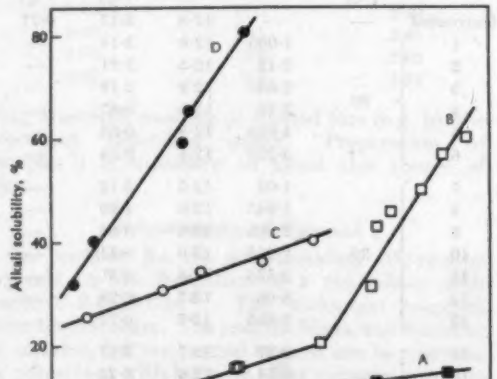
Alkali solubility, %
Acid absorbed, milliequiv./100 g fur
A H_2SO_4 and untreated fur
B HNO_3 and untreated fur (Tests 14-25)
C H_2SO_4 and pre-nitrated fur
D HNO_3 and pre-nitrated fur

FIG. 2—Effect of oxidising and non-oxidising acids at 40°C on alkali solubility of untreated and pre-nitrated fur

The second suggestion requires that nitrous acid be formed during the reaction. If this is correct, some deamination of basic side-chains would occur with the formation of nitrogen. Fur was treated with 2-N nitric acid at 40°C (liquor:fur = 5:1) and the evolution of gas was measured. The gas evolved during 22 h (at which time the evolution had ceased) was equivalent to 48·6 mmoles of nitrogen + 15·3 mmoles of carbon dioxide per 100 g of fur. The relatively large volume of nitrogen indicates that nitrous acid is formed as an intermediate product, and the fact that carbon dioxide also is produced supports the contention that the oxidation of peptide bonds is a major cause of the observed sharp increase in alkali solubility. Meunier and Pierret [20] also concluded that the presence of nitrous acid is essential in the reaction between fur and nitric acid. Moreover, the results plotted in Fig. 2 (curve D) suggest that the introduction of a nitro group into the tyrosine side-chains facilitates the oxidation of peptide bonds even more than it does their hydrolysis.

The increase in the slope of the initial part of the curves with increase in temperature (Fig. 1) is not entirely due to an increase in the extent of hydrolysis of the peptide chains, as is shown by comparison with sulphuric acid treatment (Fig. 2); at 40°C a rather greater increase in alkali solubility is caused by nitric acid (before nitration of tyrosine commences) than by an equivalent uptake of sulphuric acid. At 20°C and at 30°C these initial linear portions of curves are nearly coincident with those for sulphuric acid treatments at the same temperatures. It seemed possible that this initial increase in alkali solubility (at 40°C) might be caused by the destruction of tryptophan side-chains. However, determination of this amino acid in furs which had been treated with nitric acid at 40°C showed that the tryptophan side-chains are completely destroyed at about that concentration of nitric acid which causes nitration of tyrosine side-chains and are not affected at lower concentrations. Thus, the initial increase in alkali solubility is not due to a gradual decomposition of tryptophan with increase in acid concentration. The greater initial increase in alkali solubility caused by nitric acid as compared with sulphuric acid is therefore due to oxidation of peptide bonds, and this degradation is in addition to the hydrolysis which would be caused by both of these acids.

Fig. 3 shows that once the nitric acid concentration has reached an appropriately high value the nitration of tyrosine proceeds readily until about 87% of the tyrosine side-chains have been mono-nitrated, but thereafter appreciably higher concentrations of nitric acid are necessary in order to nitrate the remainder of the tyrosine. The remaining 13% of the tyrosine may therefore be present in a morphological component of the fibre which is comparatively resistant to chemical reagents.

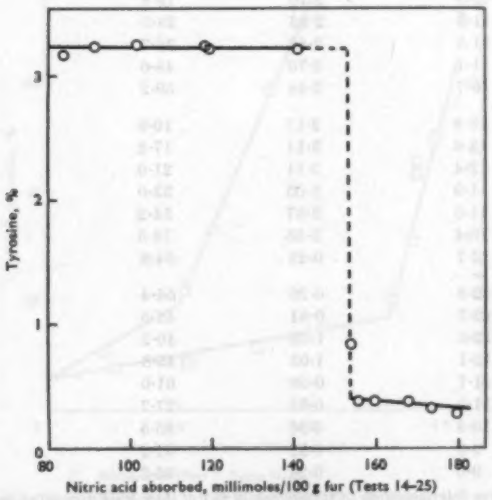

FIG. 3—Effect of absorption of nitric acid on tyrosine content of fur

Conclusions

Cystine (in fur) is not attacked by nitric acid under the conditions used for these tests; it is also unaffected when nitric acid alone is used in the carrotting process.

Tyrosine side-chains are mono-nitrated in the *ortho* position when the concentration of nitric acid and the temperature are sufficiently high. A marked increase in alkali solubility accompanies the nitration of tyrosine side-chains and there is evidence that both hydrolysis and oxidation of peptide bonds by nitric acid occur more easily after a nitro group has been introduced into the tyrosine.

Tryptophan is completely destroyed under those conditions that cause nitration of tyrosine side-chains.

No evidence has been found that the amino-acid composition of rabbit fur is otherwise affected by nitric acid under these conditions.

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A Study of the Chemistry of Carrotting Processes
II—The Effect of Hydrogen Peroxide and Nitric Acid on Rabbit Fur

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The simplest non-mercuric carrotting solution, hydrogen peroxide and nitric acid, reacts with both cystine and tyrosine in rabbit fur. There is evidence that nitrous acid is a by-product of the oxidation of cystine by these reagents and, under the special conditions which prevail inside the fur fibre, this intermediate may play an important part in subsequent reactions and especially in the nitration of tyrosine side-chains.

Introduction

Some hydrogen peroxide (in neutral solution) combines reversibly with the amino and imino groups in animal fibres [1], e.g. 100 g of wool can absorb 30 mmoles of peroxide from a 3% solution, and this may be removed completely by washing. Cystine is the first amino acid in wool to be attacked by peroxide and some sulphate is produced in this reaction [2]. Smith and Harris [3] showed that the reaction with cystine is not greatly influenced by the hydrogen ion concentration below pH 7·0. The cystine content of wool is reduced by about 0·7% on treatment with 0·18-M hydrogen peroxide (below pH 7·0) at 50°C for 3 h, and this is accompanied by an increase in the alkali solubility to 20%; at this concentration the extent to which the reaction occurs increases markedly with increase in temperature, the fibres becoming completely soluble in alkali at 80°C, while the cystine content is reduced from 11·3% to 7·4%. The acid-combining power of the fibres is decreased by this treatment.

Elöd, Nowotny, and Zahn [4] found that wool and silk (which contains no cystine) dissolve completely in 3% hydrogen peroxide at 60°C during 3 days, indicating considerable attack on peptide bonds; no peptides of high molecular weight could be detected in the solution. The reaction between wool and hydrogen peroxide is powerfully catalysed by heavy-metal ions; these can cause the rate of reaction to increase 100-fold [5]. Hydrogen peroxide in non-aqueous solution (n-amyl alcohol) has no effect on wool at 20°C; at 80°C a decrease in feltability was observed but only after extensive degradation [6]. It was concluded from this, and from other observations, that hydrogen peroxide cannot cause a decrease in the felting properties of fibres solely by surface modification. A comprehensive series of practical felting tests [7], in which a large number of solutions containing peroxide and nitric acid with additions of various metallic salts were compared with mercuric nitrate in excess of nitric acid, showed that none of the processes based on nitric acid and peroxide could increase the

TABLE I

Effect of Various Mixtures of Nitric Acid and Hydrogen Peroxide on Rabbit Fur at 40°C†

Test	$[HNO_2]_o$ (mole)	$[H_2O_2]_o$ (mole)	Cystine (%)	Tyrosine (%)	Alkali solubility (%)
Untreated	—	—	12·8	3·17	5·6
38		0·0318	12·8	3·21	9·3
39		0·0625	12·7	3·18	10·5
40		0·123	12·5	3·11	15·0
41		0·183	12·5	3·10	19·8
42	0·526	0·242	11·9	2·95	28·0
43		0·299	11·5	2·86	36·7
44		0·363	11·1	2·70	48·0
45		0·418	10·7	2·58	59·2
46†	0·215		12·8	3·17	10·9
47†	0·418		12·6	3·11	17·2
48	0·527		12·4	3·11	21·0
49	0·635	0·182	11·9	3·05	33·0
50	0·851		11·0	2·87	54·2
51	1·065		10·4	2·65	76·5
52	1·489	nil	12·7	0·29	54·8
53		nil	12·8	0·26	54·4
54		0·00574	12·7	0·81	42·5
55		0·0100	12·5	1·06	40·2
56		0·0154	12·1	1·02	45·8
57	1·495	0·0247	11·7	0·58	61·0
58		0·0497	11·0	0·38	77·7
59		0·0742	10·3	0·36	85·5
60		0·0990	9·6	0·32	91·2
61		0·124	9·0	0·31	95·2

† The tryptophan content of the untreated fur was 0·77%; the only positive determinations of tryptophan in any of these tests were given by test 46 (0·11%) and test 47 (0·03%).

rate of felting of fur as effectively as the mercuric carrotting process.

We have measured some of the chemical changes that occur when rabbit fur is treated with nitric acid and hydrogen peroxide under conditions that are similar to those used in the carrotting process.

Experimental

Reaction conditions and analytical techniques were the same as those used previously (Part I). Hydrogen peroxide in the original solutions and in the filtrates was determined by titration with permanganate. In all cases, except where otherwise stated, the fur was treated at 40°C for 20 h.

Results and Discussion

Some of the changes that occur when rabbit fur is treated with nitric acid and hydrogen peroxide of various concentrations are indicated in Table I. When both nitric acid and peroxide are present, reaction occurs with the combined cystine, tyrosine, and tryptophan in fur. Examination of the hydrolysates of treated furs by means of paper chromatography did not reveal any significant change in other amino acids. These results do not agree with those of Fröhlich [8], who found that tyrosine was no longer detectable when 30–50% of the tryptophan had been destroyed; he also observed an appreciable reduction in the proportion of valine, phenylalanine, leucine, proline, and alanine. The extent of reaction, as measured by the alkali solubility, suddenly increases when the total initial concentration of reactants exceeds that value which is required to produce an alkali solubility of about 20% (Fig. 1). A similar behaviour was observed when fur was treated with nitric acid alone, but in this case the concentration of reactant required to cause this sharp increase in alkali solubility was appreciably higher (Part I). Small amounts of 3-nitrotyrosine were detected in some of the hydrolysates from tests 38–51.

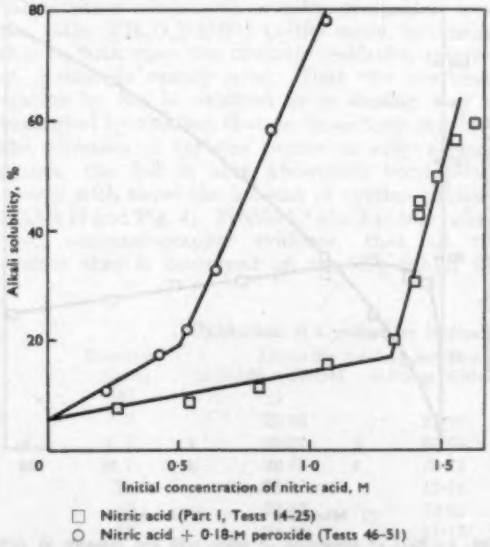

FIG. 1— Effect of initial reagent concentration on alkali solubility of fur

In tests 52–61 the initial concentration of nitric acid alone was high enough to cause nitration of most of the tyrosine, but the addition of small amounts of hydrogen peroxide decreased the extent of nitration of the tyrosine side-chains (Fig. 2) and the effect of this was also reflected in the alkali solubility (Fig. 3). At higher concentrations of peroxide (> 0·015 M) attack on the tyrosine side-chains increased until at about 0·1 M this reaction occurred to almost the same extent as in the absence of peroxide. In all these tests (52–61) the only yellow compound in the hydrolysates that could be detected by paper chromatography was 3-nitrotyrosine, and the determinations of this product were in good agreement with the change in the tyrosine content of the furs caused by the treatment.

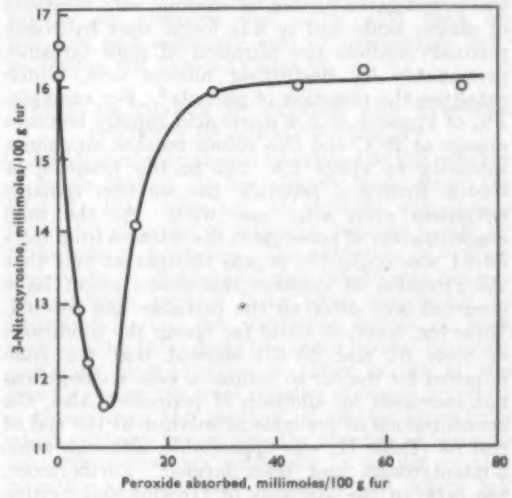

FIG. 2— Inhibiting effect of peroxide on nitration of tyrosine in fur (Tests 52–61)

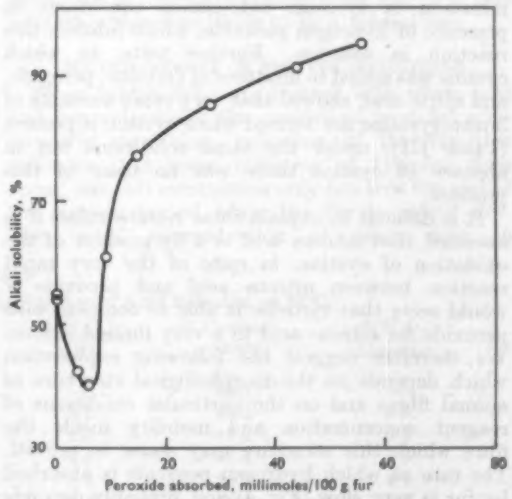

FIG. 3— Effect of 1·5-M nitric acid and peroxide at 40°C for 20 h on alkali solubility of fur (Tests 52–61)

TABLE II

Change in Chemical Composition of Fur during Reaction with Nitric Acid and Hydrogen Peroxide at 40°C

Initially, $[HNO_3] = 0.518$ M and $[H_2O_2] = 0.466$ M

Test	Time (h)	Cystine (%)	Tyrosine (%)	$\frac{\Delta \text{ tyrosine}}{\Delta \text{ cystine}}$	Alkali solubility (%)
Untreated	0	12·8	3·17	—	5·6
62	1	12·7	3·16	—	6·8
63	2	12·6	3·17	—	8·1
64	4	12·5	3·14	—	11·2
65	7	12·3	3·08	0·18	16·8
66	12	11·6	2·88	0·24	31·6
67	16	11·2	2·81	0·22	40·8
68	20	10·4	2·75	0·18	70·1
69	26	9·8	2·75	0·14	79·9

INHIBITION OF NITRATION OF TYROSINE BY PEROXIDE

The unexpected effect illustrated in Fig. 2 and 3 was investigated further by working with solutions of amino acids and it was found that hydrogen peroxide inhibits the nitration of pure tyrosine, presumably by destroying nitrous acid, which catalyses the nitration of phenols [9]. For example, 1% of tyrosine in 2-M nitric acid rapidly becomes orange at 20°C and this colour reaches maximum intensity in about 2 h, but in the presence of 0·01-M hydrogen peroxide the solution remains colourless even after one week. As the final concentration of peroxide in the filtrates from tests 54–61 was negligible, it was thought at first that the nitration of tyrosine side-chains might have occurred only after all the peroxide had reacted. However, tests on white fur (using the conditions of tests 53 and 58–61) showed that the time required for the fur to assume a yellow colour was not increased by addition of peroxide. Also, the concentration of peroxide in solution at the end of test 68 (Table II) was appreciable, although some 3-nitrotyrosine had been formed. Furthermore, the ratio of the amounts of tyrosine and cystine that had reacted did not increase during the course of the reaction (Table II).

It was therefore necessary to explain how nitration of tyrosine side-chains can occur in presence of hydrogen peroxide, which inhibits this reaction in solution. Further tests, in which cystine was added to mixtures of tyrosine, peroxide, and nitric acid, showed that very small amounts of 3-nitrotyrosine are formed when cystine is present (Table III); under the same conditions but in absence of cystine there was no trace of this product.

It is difficult to explain these results unless it is assumed that nitrous acid is a by-product of the oxidation of cystine; in spite of the very rapid reaction between nitrous acid and peroxide it would seem that tyrosine is able to compete with peroxide for nitrous acid to a very limited extent. We therefore suggest the following explanation which depends on the morphological structure of animal fibres and on the particular conditions of reagent concentration and mobility inside the fibre which this structure may cause to prevail. The rate at which hydrogen peroxide is absorbed by fur is very slow (Fig. 4) and probably depends on the rate of diffusion into or through the fibre.

TABLE III

Formation of 3-Nitrotyrosine in Presence of Peroxide and Cystine during 19 h at 40°C

Initially, [tyrosine] = 0·01 M, $[HNO_3] = 1.5$ M and [cystine] = 0·01 M

$[H_2O_2]_0$ (mole/l.)	3-Nitrotyrosine (mmole/l.)
nil	9·8
0·01	nil
0·02	0·07
0·05	0·14
0·10	0·25
0·15	0·35
0·20	0·49

The concentration of peroxide inside the fibre may therefore be small enough to permit the existence of some nitrous acid, especially under these conditions that restrict the movement of molecules and ions. As the influence of nitrous acid on the nitration of tyrosine is catalytic, very small concentrations could have a marked effect. The small concentrations of peroxide which cause the effect illustrated in Fig. 2 and 3 may be sufficient to destroy some of the nitrous acid formed during the oxidation of a few peptide links, while being insufficient to cause much reaction with cystine

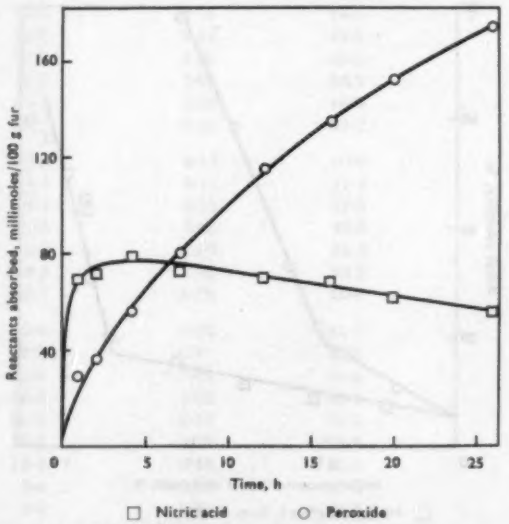

FIG. 4—Rate of absorption of nitric acid and peroxide at 40°C (Tests 62–69)

and hence the (assumed) production of nitrous acid.

OXIDATION OF CYSTINE BY PEROXIDE IN ACID SOLUTION

The concentration of nitric acid in solution at the end of tests 38–45 increased as the initial concentration of peroxide was increased. Absence of nitrogen evolution in all tests in Tables I and II showed that deamination was not occurring; therefore, acid groups were being produced during the reaction. Oxidation of cystine by peroxide in acid solution was investigated. The results in Table IV show the relative quantities of peroxide used and acid produced during a typical run.

TABLE IV

Oxidation of Cystine by Peroxide in Nitric Acid Solution at 50°C

Initially, [cystine] = 0·0501 M

Reaction time (h)	Titres for 5·00-ml samples 0·100-N NaOH	0·101-N $KMnO_4$	$\Delta[H_2O_2]/\Delta[H^+]$
0	21·74	19·45	—
5	22·12	17·23	2·9
8	22·35	16·44	2·5
24	22·99	12·86	2·7
48	23·76	9·01	2·6
72	24·37	6·44	2·5
96	24·78	4·53	2·5

The acid concentration was measured potentiometrically. Peroxide was determined by titration with permanganate after neutralising the sample and acidifying slightly with acetic acid; these titration conditions did not cause oxidation of unchanged cystine by permanganate. Because it was not possible to determine cystine in presence of nitric acid, similar tests were carried out using sulphuric acid (Table V).

The results in Table V suggest that the overall reaction may be represented by the equation—

$$R\text{–}S\text{–}S\text{–}R + 5H_2O_2 \rightarrow 2R\text{–}SO_3H + 4H_2O$$

When either nitric acid or sulphuric acid is used the ratio $\Delta[H_2O_2]/\Delta[H^+]$ is the same, indicating that in both cases the ultimate oxidation product of cystine is cysteic acid. That the combined cystine in fur is oxidised in a similar way is supported by the fact that, in those tests in which the nitration of tyrosine occurs to only a small extent, the fall in acid absorption corresponds closely with twice the amount of cystine oxidised (Table II and Fig. 4). Fröhlich [8] also has concluded, from chromatographic evidence, that all the cystine that is destroyed on treating rabbit fur with peroxide and nitric acid can be accounted for as cysteic acid.

Although the overall oxidation of cystine may be represented by the above equation, this reaction occurs in several stages [10, 11] and there is evidence that the intermediate oxidation products are also formed when wool is treated with peroxide [3]. It has already been shown that nitrous acid is a by-product of the oxidation of cystine by peroxide in presence of nitric acid. Moreover, nitric acid alone does not attack cystine in fur under the conditions used (Part I). All this evidence suggests that hydrogen peroxide is involved in the initial attack on cystine and that nitric acid takes part in a subsequent step; the nitrous acid so formed would be oxidised rapidly by peroxide and the participation of nitric acid would not therefore affect the overall equation. This interpretation is supported by the fact that cystine is oxidised more rapidly by peroxide and nitric acid than by peroxide and sulphuric acid of comparable concentration (cf. Tables IV and V).

EFFECT OF CHANGE IN CYSTINE AND TYROSINE CONTENTS ON ALKALI SOLUBILITY

Alkali solubility should be related to the number of bonds broken. It has already been shown (in Part I) that nitration of tyrosine side-chains facilitates cleavage of adjacent peptide bonds by hydrolysis or oxidation. The oxidation of cystine cross-links to cysteic acid side-chains also renders the adjacent peptide links more susceptible to hydrolysis [12], i.e. the oxidative fission of each cystine cross-link affects two other bonds. Ignoring oxidation or hydrolysis at other points in the peptide chain, the total number of bonds involved is three times the number of cystine cross-links which undergo fission plus the number of tyrosine side-chains that are nitrated. In a plot of this quantity against alkali solubility, all points fall near a smooth curve (Fig. 5). It may be noted that the results plotted in Fig. 5 include not only a wide range of reagent concentrations and ratios but also variations in time of treatment from 1 to 25 h; this relation is therefore likely to be a general one.

THE IMPORTANCE OF STOVING CONDITIONS

When rabbit skins are treated with nitric acid and peroxide under the conditions used for non-mercuric carrotting, yellowing of the fur tips indicates that some nitration of tyrosine does occur, but this commences only towards the end of the stoving period when the fur is nearly dry. The initial concentration of nitric acid in

TABLE V

Oxidation of Cystine by Peroxide in Sulphuric Acid Solution at 50°C

Reaction time (h)	Titres for 5·00-ml samples 0·100-N NaOH	0·101-N $KMnO_4$	$\frac{\Delta[H_2O_2]}{\Delta[H^+]}$	Cystine (mM)	$\frac{\Delta[H_2O_2]}{\Delta[\text{cystine}]}$
0	22·33	21·08	—	50·1	—
5	22·52	20·30	2·1	48·4	4·6
8	22·63	19·72	2·3	47·5	5·3
24	23·12	17·16	2·5	41·4	4·6
48	23·85	13·83	2·4	35·0	4·7
72	24·40	11·18	2·4	30·8	5·2
96	24·93	8·66	2·4	26·1	5·2

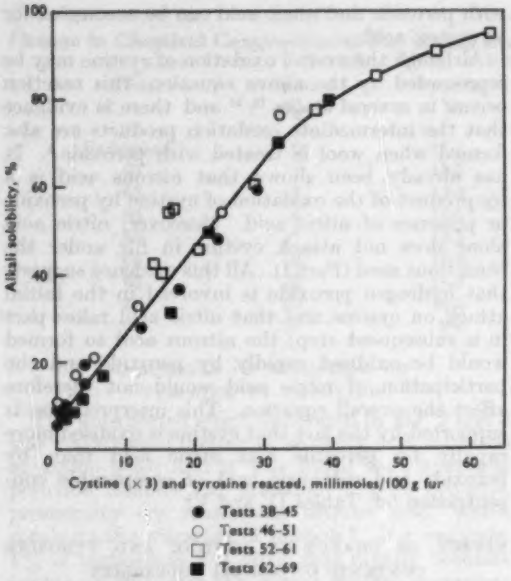

FIG. 5—Relation between alkali solubility of fur and amounts of cystine and tyrosine reacted

commercial carrotting solutions usually lies in the range 0·5–1·5 M, and this concentration must increase considerably during stoving. The concentration of nitric acid required to cause nitration of tyrosine at the temperature of the liquid on the skins (this is always much lower than the air temperature in the stove) will certainly be reached. Hydrogen peroxide is usually present initially at a concentration of between 0·5 and 2 M. The highest

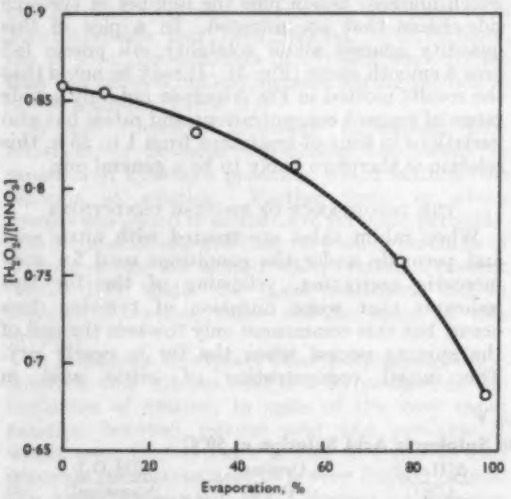

FIG. 6—Effect of evaporation on composition of reagents in non-mercuric carrotting solution

concentrations in this range do produce a fur which is less yellow, presumably because the concentration of peroxide inside the fibre is then sufficient to cause some inhibition of the nitration of tyrosine. Stoving conditions may play an important part not only because change in temperature will affect rates of reaction and diffusion to different degrees, but also because of the different rates of evaporation of nitric acid and peroxide from a mixture. In tests in which a mixture of these two reagents in a shallow glass dish was evaporated by a current of warm air from a hair dryer, we have found that hydrogen peroxide evaporates rather more rapidly than nitric acid (Fig. 6); the temperature of the air close to the liquid surface was 50 ± 1°C.

Conclusions

On the present evidence, we suggest that the following changes occur when rabbit fur is subjected to those non-mercuric processes which involve treatment with nitric acid and peroxide—

Nitric acid penetrates rapidly and hydrogen peroxide slowly into the fibres.

Reaction between nitric acid and tyrosine side-chains forms 3-nitrotyrosine side-chains. This reaction occurs readily at concentrations of nitric acid above about 1·4 M at 40°C, but also to a limited extent at much lower concentrations of nitric acid in presence of peroxide.

Reaction between hydrogen peroxide and cystine cross-links forms cysteic acid side-chains. Nitric acid can also take part in this oxidation and the nitrous acid so formed can influence the nitration of tyrosine side-chains.

Acid hydrolysis and oxidation of peptide bonds occur, facilitated by the introduction of a nitro group into the tyrosine side-chain and by the formation of cysteic acid side-chains.

Tryptophan is destroyed by nitric acid at concentrations greater than 0·5 M at 40°C in presence of peroxide.

The extent to which these reactions occur in practice is dependent on the stoving conditions to which the carrotted skins are subjected, e.g. temperature will affect the rates of diffusion into the fibre and of chemical reaction in the fibre, and humidity conditions will affect the rate of evaporation, which in turn affects not only the overall rate at which reactants are concentrated but also their relative proportions because they evaporate at different rates.

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A Study of the Chemistry of Carrotting Processes
III—The Effect of Mercuric Nitrate and Nitric Acid on Rabbit Fur

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The complex reactions that occur when rabbit fur is treated with a solution of mercuric nitrate in dilute nitric acid involve both cystine cross-linkages and tyrosine side-chains. Nitrous acid is an important intermediate. Mercuric nitrate and nitric acid attack tyrosine side-chains far more effectively than do mixtures of hydrogen peroxide and nitric acid at comparable concentrations; this may be one reason for the superior felting properties of mercuric-carrotted furs as compared with non-mercuric-carrotted furs. The evolution of carbon dioxide and nitrogen from cystine and from fur during treatment with these reagents has not been reported previously. The observations reported in the three papers in this series are discussed.

Introduction

The extent to which mercuric salts react with wool depends largely on the conditions employed. The rate of hydrolysis of wool by water is greatly accelerated by finely divided metallic mercury and a soluble mercuric salt[1], e.g. 50% of the sulphur in wool was removed (as sulphide) during 2–3 days at 80°C, but the tensile strength of the dry fibres was unaffected by this extensive modification. Speakman and Coke[2] found that mercuric chloride is strongly absorbed by the amino groups in wool, but cystine cross-links are not affected by this reagent at room temperature; using very similar conditions, Elöd[3] detected a very slow reaction with the cystine in wool. Treatment with mercuric chloride does not lead to the formation of any new cross-linkages and in this respect mercuric chloride differs from mercuric acetate, which causes an increase in the work required to extend the treated fibres. At 40°C mercuric salts cause fission of disulphide bonds, but they can also form new cross-linkages at points where bonds have been broken by acid attack. Barr and Speakman[4] observed that the bond-forming capacity of mercuric acetate is decreased by strong mineral acids; they suggested that in the mercuric carrotting process there is a balance between acid hydrolysis and bond-building by divalent mercury.

The reaction between animal fibres and mercuric salts in presence of nitric acid has been studied by a number of workers. Millon's reagent (which is essentially the same as a mercuric carrotting solution except that the concentration of nitrous acid may be appreciably higher, depending on the method of preparation) was found by Stoves[5] to contract the length of a human hair, according to the duration of the treatment, and this contraction was further increased by immersing the treated fibre in boiling water. He suggested that cross-linkages containing mercury are unstable and that this effect is connected with the spontaneous curling of carrotted fibres in boiling water[6]. Meunier and Pierret[7] stated that pure nitric acid (free from nitrous acid) has no action on fur; they consider that carrotting depends on deamination by nitrous acid followed by formation of cross-linkages by mercuric salts. As the concentration of a mercuric carrotting solution is increased, the decrease in the cystine content of fur is accompanied by a decrease in alkali solubility; this is explained by assuming that a higher concentration of mercury causes bond formation between amide and carboxylic acid groups[8]. Geerts and t'Jampens[9] have compared the action of mercuric nitrate and nitric acid on fur with that of mercuric chloride, hydrochloric acid, and hydrogen peroxide; they believe that similar reactions occur in these treatments and that mercuric carrotting consists in oxidising part of the cystine with nitric acid while the rest of the cystine is protected by mercury; catalysis by mercuric salts may assist oxidation of the cystine. Fröhlich[10] has used end-group analysis to show that mercuric carrotting solutions cause rupture of peptide linkages where serine occurs in the main chain; he believes that, in addition to the attack on cystine, mercury also reacts with amide and carboxyl groups, as well as with aliphatic and phenolic hydroxyl groups in fur.

The present investigation is concerned with the changes in the chemical composition of rabbit fur caused by mercuric nitrate and dilute nitric acid and with some of the reactions which lead to these changes.

Experimental

The raw material and the conditions of treatment were similar to those used in Part I. The solutions were prepared from nitric acid and red mercuric oxide of analytical reagent grade. Mercuric ions in solution were determined by titration with standard ammonium thiocyanate using ferric alum indicator.

When nitric acid is titrated with standard sodium hydroxide in presence of mercuric ions, the end-point is obscured by precipitation of mercuric oxide. We have found that the addition of sodium chloride (5 ml of 4 M) prevents the formation of a precipitate and gives a well-defined end-point (bromophenol blue indicator) which corresponds to the amount of free nitric acid present initially. Incidentally, this procedure provides an excellent method for the routine analysis of mercuric carrotting solutions.

Mercuric ions (in the amounts present in these tests) do not affect the determination of cystine and tyrosine (by the methods used in Part I) so long as the treated furs are washed very thoroughly to remove traces of nitrate. The results recorded here for the determinations of cystine, tyrosine, and alkali solubility are corrected to allow for the weight of mercury present in the treated fur (i.e. all results are expressed as percentages on the original weight of fur). Acid concentrations and amounts absorbed are calculated from the results of the titration of the free acid in solution.

TABLE I

Reaction of Fur with Mercuric Nitrate and Nitric Acid at 40°C

Initially, $[HNO_3]$ = 0·261 M and $[Hg^{++}]$ = 0·0899 M

Test	Reaction time (h)	Reactants absorbed HNO_3 (mmole/100 g fur)	Reactants absorbed Hg^{++} (mmole/100 g fur)	Cystine (%)	Tyrosine (%)	Alkali solubility (%)
Untreated	0	—	—	12·8	3·17	5·6
70	0·5	71·5	10·0	12·6	3·06	18·4
71	1	62·0	16·7	12·2	3·00	22·3
72	2	54·5	26·0	11·6	2·74	29·0
73	4	49·7	34·0	10·9	2·55	36·0
74	6	47·3	39·1	10·8	2·54	39·5
75	20	42·2	47·4	10·2	2·52	48·0

TABLE II

Effect of Various Concentrations of Mercuric Nitrate and Nitric Acid on Fur at 40°C

Test	$[HNO_3]_0$ (M)	$[Hg^{++}]_0$ (M)	Reactants absorbed HNO_3 (mmole/100 g fur)	Reactants absorbed Hg^{++} (mmole/100 g fur)	Cystine (%)	Tyrosine (%)	Alkali solubility (%)
	nil	nil	—	—	12·8	3·17	5·6
76	0·369	0·0277	77·0	14·8	12·3	3·00	16·9
77		0·0549	72·5	28·6	10·9	2·67	29·2
78		0·0825	65·1	45·2	9·1	2·20	52·1
79		0·111	55·0	60·5	8·4	1·65	74·5
80		0·138	38·1	76·0	8·0	1·35	89·0
81	0·0618	0·0642	18·0	33·0	11·4	3·10	27·4
82	0·341		62·0	33·6	11·1	2·86	41·5
83	0·554		98·7	33·4	10·8	1·08	58·5
84	0·758		109·4	33·8	10·3	0·47	73·5
85	0·942		120·2	34·3	9·4	0·30	83·3
86	1·13		134·0	34·3	8·3	0·25	93·5

Results

The rate of absorption of nitric acid and of mercuric ions by fur at 40°C was measured and the results are shown in Table I. The uptake of mercuric ions is slow and probably depends on the rate of diffusion into the fibres. Absorption of acid is very rapid initially, but this is followed by a slow increase in the concentration of acid in solution; this subsequent decrease in acid absorption is due to deamination and to the formation of acidic side-chains from cystine (see later).

Tests 76–80 in Table II show the effect of increasing the initial mercuric ion concentration at a constant initial acid concentration, and tests 81–86 commence with the same concentration of mercury in solution while the nitric acid concentration is increased. Some 3-nitrotyrosine was detected in the hydrolysates from tests 83–86.

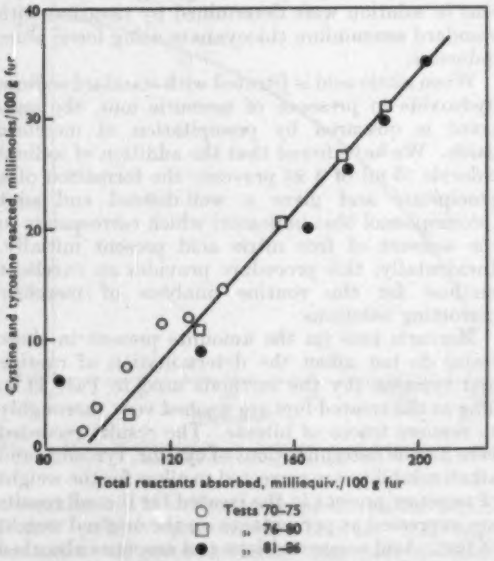


FIG. 1— Relation between amount of reagents absorbed by fur and change in cystine and tyrosine contents

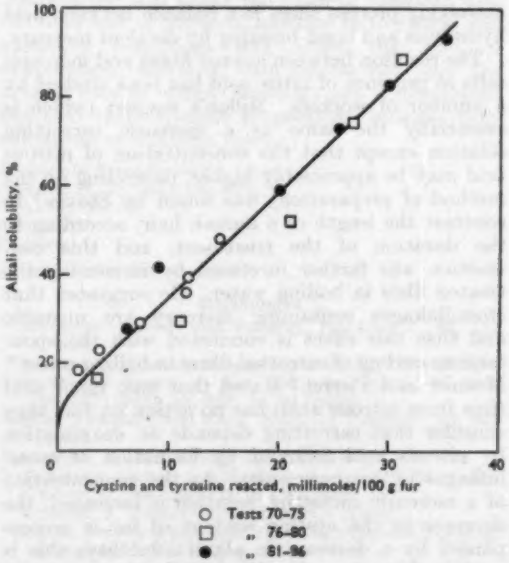


FIG. 2 — Relation between alkali solubility and change in cystine and tyrosine contents

The total amount of cystine and tyrosine that had reacted (in the tests in Tables I and II) is approximately related to the combined amounts of the reactants used (Fig. 1) and to the alkali solubility (Fig. 2). However, the reactions are not as simple as these relationships might suggest. As both cystine cross-links and tyrosine side-chains are affected by these treatments, the reactions of these two amino acids in solution were next studied.

REACTION BETWEEN CYSTINE AND MERCURIC NITRATE IN DILUTE NITRIC ACID

In presence of the minimum amount of nitric acid required to dissolve the reactants, cystine and mercuric ions react rapidly to give a white precipitate (I) and some nitrous acid. The washed precipitate, on being treated with 4-M nitric acid at 20°C, slowly assumes a translucent appearance; during this change, part of the mercury goes into solution (the residue is referred to as substance II).

$$\text{Cystine} + \text{mercuric ions} \xrightarrow{\text{nitric acid}} \text{I} + \text{nitrous acid} \quad \ldots\ldots (1)$$

$$\text{I} + \text{nitric acid (4 M)} \longrightarrow \text{II} + \text{mercuric ions} \quad \ldots\ldots (2)$$

These reactions were studied in greater detail.

Ratio of Cystine to Mercuric Ions in Reaction 1

Mercury was determined (by titration with thiocyanate) in the filtrates from mixtures containing various concentrations of reactants (Table III). The results in the last column show that two mercuric ions react with one molecule of cystine.

TABLE III

Reaction between Cystine and Mercuric Nitrate in 0·1-M Nitric Acid

Initial concentrations Hg^{++} (M)	Cystine (M)	Hg^{++} in filtrate* (M)	Hg^{++}/cystine in precipitate
0·0238	0·0024	0·0184	2·2
0·0233	0·0034	0·0161	2·1
0·0227	0·0046	0·0127	2·2
0·0218	0·0063	0·0089	2·0
0·0208	0·0083	0·0036	2·1
0·0195	0·0107	nil	—
0·0178	0·0143	nil	—

* The solutions were filtered after 1 h at 20°C.

Determination of Nitrous Acid Produced in Reaction 1

Nitrous acid was determined by a method based on the coupling of diazotised sulphanilic acid with 1-naphthylamine [11]. The concentration of nitrous acid present during the reaction is shown in Fig. 3. Nearly all the nitrous acid is formed during the first ten minutes after mixing the reactants, but it is decomposed slowly by reaction with the amino groups in cystine, with evolution of nitrogen. Extrapolation of the decomposition portion of the curve to zero time should give approximately the total amount of nitrous acid produced in the reaction. When this amount of nitrous acid (from sodium nitrite) was treated with cystine in nitric acid (i.e. under the same conditions except that mercuric ions were absent) and the change in the nitrous acid concentration was measured at intervals, the concentration/time curve (Fig. 3) corresponded closely with the extrapolated decomposition curve for the nitrous acid produced in the mercury/cystine reaction; these results indicate that one molecule of nitrous acid is produced in the reaction between two mercuric ions and one molecule of cystine.

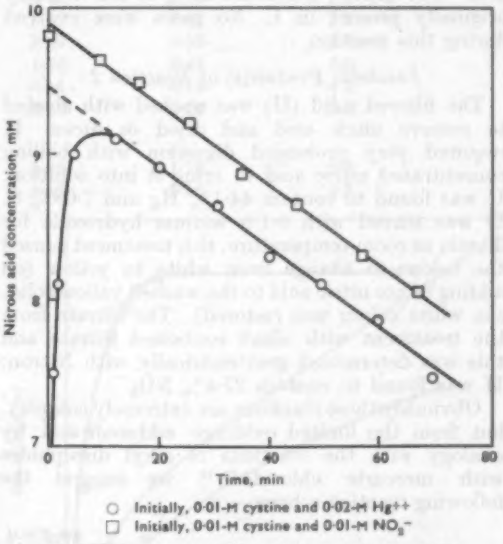


FIG. 3 — Formation and decomposition of nitrous acid in 2-M nitric acid at 20°C

Insoluble Product(s) of Reaction 1

In order to prevent reaction of the amino groups in the insoluble product with nitrous acid, the precipitate (I) was filtered off after the reaction mixture had stood for only 5 min. After being washed and dried *in vacuo*, the precipitate was decomposed by refluxing with concentrated nitric acid; prolonged digestion (20–40 h) was required to effect complete dissolution. Mercury was determined in the digest by titration with thiocyanate; I contained 58·2% Hg. Sulphur was determined as barium sulphate after evaporation and oxidation of the residue [12]; I was found to contain 7·97% S, which represented 72% of the sulphur originally present in the cystine.

Two other interesting observations concerning the reactions of this product were that it was slowly decomposed by dilute sodium hydroxide to give a yellow solution and mercuric sulphide, and that it dissolved completely on being warmed with dilute hydrochloric acid to give a solution which contained an appreciable amount of cysteine.

Soluble Product(s) of Reaction 1

The filtrate from reaction 1 did not contain sulphate. When the filtrate was evaporated and the residue digested with concentrated nitric acid, the sulphur, determined as barium sulphate, accounted for the remaining 28% of the sulphur in the original cystine, i.e. the sulphur in the filtrate was present as a soluble organic compound. The neutralised filtrate (after desalting) was examined

by means of paper chromatography; two brown spots were developed after treating the chromatograms with ninhydrin, one of which was identified as cysteic acid.

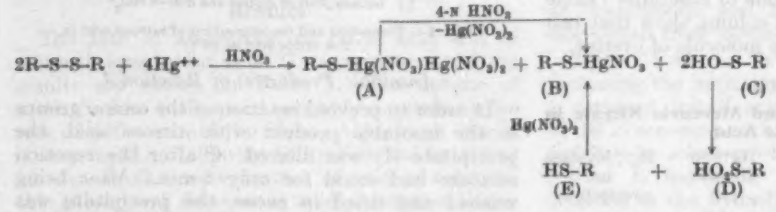
Elimination of Mercuric Ions in Reaction 2

I was treated with 4-N nitric acid at 20°C for 16 h and then filtered and washed with 4-N nitric acid. The filtrate contained 27% of the mercury originally present in I. No gases were evolved during this reaction.

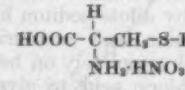
Insoluble Product(s) of Reaction 2

The filtered solid (II) was washed with alcohol to remove nitric acid and dried *in vacuo*. II required very prolonged digestion with boiling concentrated nitric acid to bring it into solution. It was found to contain 44·1% Hg and 7·08% S. II was stirred with 0·1-N sodium hydroxide for 30 min at room temperature; this treatment caused the colour to change from white to yellow (on adding dilute nitric acid to the washed yellow solid, the white colour was restored). The filtrate from the treatment with alkali contained nitrate and this was determined gravimetrically with Nitron; II was found to contain 27·4% NO_3^-.

Obviously these reactions are extremely complex, but from the limited evidence adduced and by analogy with the reactions of alkyl disulphides with mercuric chloride[13,14] we suggest the following reaction scheme—



The insoluble product of reaction 1 may have contained A, B, and possibly some mercaptide from E because the acid concentration was low. The results of the analysis of this product may not be very useful because some nitrate groups may have been hydrolysed during the washing. The final product of reaction 2 is B and, as hydrolysis of nitrate groups was avoided by washing with alcohol, the analysis is more reliable and the results are in good agreement with the structure

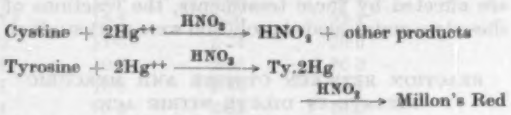


Nitrous acid could be formed during nitric acid oxidation at the sulphur atom of any of these products.

REACTION OF TYROSINE WITH MERCURIC NITRATE IN DILUTE NITRIC ACID

In dilute solution at 40°C and with mercuric nitrate in excess of tyrosine, a colourless crystalline compound was formed very slowly; this was found to contain one mole of tyrosine and two moles of mercury. On treating this compound with nitrous acid an intense red colour was produced; this, according to Lugg[15], is Millon's Red. The same colour is produced when cystine is added to a solution of tyrosine and mercuric nitrate in nitric acid, i.e. the nitrous acid is formed in the mercury/cystine reaction.

The reactions which occur in the presence of both amino acids may therefore be represented as—



Some 3-nitrotyrosine may also be formed if the concentration of nitric acid is sufficiently high.

REACTION OF FUR WITH MERCURIC NITRATE IN DILUTE NITRIC ACID

It may now be considered whether those reactions which have been investigated in the preceding sections also occur when fur is treated with the same reagents under the same conditions. Fortunately, the several characteristic features of these reactions enable a comparison to be made, and the following evidence suggests that the same (or very similar) reactions occur in fur fibres.

(1) Fur treated with mercuric nitrate and nitric acid develops a red colour (Millon's Red) even when the reagents are first boiled to remove traces of nitrogen oxides. Moreover, pretreatment of the fibres with urea, a reagent which destroys nitrous acid, prevents the formation of the red colour.

(2) When mercuric-carrotted fur is digested with concentrated nitric acid (e.g. for the determination of sulphur) the clear liquid that remains after the protein has been destroyed contains small quantities of a white insoluble material which is rendered soluble only by prolonged refluxing (cf. substances I and II).

(3) Mercuric-carrotted white fur assumes a dirty grey appearance on being treated with alkali during the determination of alkali solubility. Substances I and II slowly blacken in 0·1-N sodium hydroxide at 65°C owing to the formation of mercuric sulphide.

(4) It is not possible to determine nitrous acid directly in the reaction between fur and mercuric nitrate because nitrous acid formed inside the fibre would react with free amino groups, with evolution of nitrogen. If nitrous acid is formed in fur in appreciable quantities (as it is when cystine is treated under the same conditions) then, because only small amounts of nitrous acid are involved in the formation of Millon's Red and in catalysing the nitration of tyrosine, nearly all of it should react with amino groups; the resulting evolution of nitrogen should be roughly indicative of the amount of nitrous acid formed in the reactions in fur.

The evolution of this gas from fur and from cystine in solution was measured by connecting the reaction vessel to a water-jacketed gas burette.

TABLE IV

Evolution of Gases at 40°C

Initial volume of solution for all tests = 20 ml

All solutions contained, initially, 1·0 millimoles of $Hg(NO_3)_2$

Test	Initial quantities		Evolution in 22 h		N_2 evolved / CO_2 evolved
	Cystine (mmole)	Nitric acid (mmole)	Nitrogen (mmole)	Carbon dioxide (mmole)	
a	2·0	8·0	0·54	0·16	3·4
b		16·0	0·65	0·37	1·7
c		22·0	3·19	1·87	1·7
d			3·28	1·93	1·7
f	1·0	30·0	1·76	0·88	2·0
g	0·5		0·56	0·13	4·3
j		78·0	0·43	0·15	2·9
	Fur (g)				
e	3·4	30·0	3·82	1·73	2·2
h		22·0	2·56	1·12	2·3

At the end of each test the gas in the reaction vessel was displaced by dilute nitric acid and analysed in an Orsat apparatus. Qualitative examination by standard methods[16] showed the presence of carbon dioxide only, and the remainder was assumed to be nitrogen. The results in Table IV show that increasing the initial concentrations of cystine and nitric acid (relative to the concentration of mercury) causes a marked increase in the volume of gas evolved. The ratio of cystine to mercury required for formation of product I (Table III) indicates the approximate quantity of nitrogen which would be expected from the previous determinations of nitrous acid (Table IV, test *g*).

The evolution of much larger volumes of nitrogen in presence of larger amounts of cystine (relative to mercury) was not due to the availability of more amino groups in the excess of cystine, as was shown by adding 3 millimoles of alanine to the same quantities of reagents as were used in test *g*; the total volume of gas and the proportion of nitrogen present were unaffected by this addition. The large volumes of gases evolved in tests *c* and *d* were shown to be due to a reaction between I and cystine, e.g. 0·345 g of I and 0·36 g of cystine in 1·6-N nitric acid at 40°C gave 3·8 millimoles of nitrogen and 2·3 millimoles of carbon dioxide in 22 h; relatively large quantities of nitrous acid were produced in this reaction.

The evolution of gas from 3·4 g of fur (equivalent to 1·8 millimoles of cystine) was initially slower than from pure cystine (because of the slow rate of penetration of mercuric ions into the fibres), but the total volume of gas was roughly the same after 24 h. Evolution from fur was still considerable at this time, while evolution from cystine in solution was virtually complete (Fig. 4).

The composition of the gas evolved during 22 h in various tests is shown in Table IV. In all cases where an excess of cystine (or fur) was present and the acid concentration was sufficiently high, the ratio N_2 evolved/CO_2 evolved was approximately 2 and, as each amino group on reacting with nitrous acid gives one molecule of nitrogen, it appears that about twice as many amino groups as carboxylic acid groups were being decomposed.

Normally, amino acids yield only nitrogen on being treated with nitrous acid, but it appears

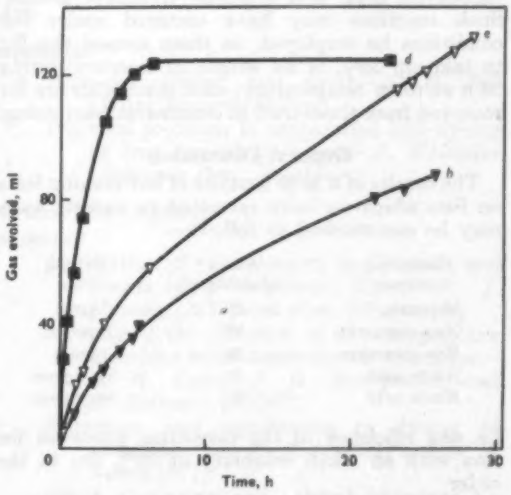


FIG. 4—Evolution of gas from fur and from cystine in presence of mercuric nitrate and nitric acid (see Table IV)

that, when cystine reacts with mercuric ions and undergoes fission, part of the product is so modified either by oxidation at the sulphur atom or by combination with mercury that deamination is accompanied by decarboxylation. In fur, where the amino groups and carboxylic acid groups of cystine are incorporated in peptide bonds, those side-chains derived from cystine which have been similarly modified may so weaken the adjacent peptide bonds that these undergo oxidative fission under the influence of nitric acid with the production of carbon dioxide.

The results of this investigation lead us to believe that the process of mercuric carrotting essentially involves the following steps—

(1) Rapid absorption of nitric acid and slow absorption of mercuric ions.

(2) Rapid reaction between the absorbed mercuric ions and cystine cross-links to yield cysteic acid (ultimately), nitrous acid, and one or more of several possible side-chains containing sulphur and mercury (perhaps with the sulphur in an oxidised state).

(3) Reaction between mercuric ions and tyrosine side-chains to give a product which reacts

rapidly with nitrous acid (from the mercury/cystine reaction) to give Millon's Red.

(4) Reaction between free amino groups and nitrous acid, with evolution of nitrogen.

(5) Oxidation of those weakened peptide bonds that are adjacent to some of the side-chains produced in the cystine/mercury reaction; the evolution of carbon dioxide as well as nitrogen is associated with this reaction.

(6) In addition to these reactions, some tyrosine side-chains may be nitrated during stoving when the concentration of nitric acid becomes sufficiently high.

We have not found any evidence that mercury combines with other side-chains in rabbit fur under normal carrotting conditions. Fröhlich[19] has suggested that mercury reacts with amide, carboxylic acid, and aliphatic hydroxyl groups. Such reactions may have occurred under the conditions he employed, as these caused the fur to take up 35% of its weight of mercury during 24 h at room temperature; such conditions are far removed from those used in commercial carrotting.

General Discussion

The results of a large number of hat-making tests on furs which we have carrotted in various ways may be summarised as follows—

Carrotting process	Alkali solubility (%)	Felting rate
Mercuric	20	good
Non-mercuric	20	poor
Non-mercuric	32	good
Nitric acid	20	very poor
Nitric acid	32	very poor

i.e. the efficiency of the carrotting processes for furs with an alkali solubility of 20% lies in the order

$$\text{mercuric} > \text{non-mercuric} \gg \text{nitric acid}.$$

The effectiveness of the reagents in producing an increase in alkali solubility may be compared from the results reported in the three papers in this series; again the same order is observed (Fig. 5).

The reactions involved in these treatments may be summarised briefly as follows—

Reagent(s)	Reaction sites
Nitric acid	Tyrosine side-chains and peptide bonds
Mercuric carrotting solutions Non-mercuric carrotting solutions	Tyrosine side-chains, cystine cross-links, and peptide bonds

In all cases the attack on peptide bonds is probably dependent to a greater or lesser extent on the modification of side-chains and on the weakening of adjacent peptide bonds which these modifications cause. Good carrotting (i.e. that which effectively increases felting rate) appears to depend on reaction at two points in the protein molecule (i.e. cystine and tyrosine). In this connection it may be noted that treatment with peracetic acid, a reagent which oxidises cystine specifically, does increase the felting rate but not to the same extent as the conventional mercuric and non-mercuric

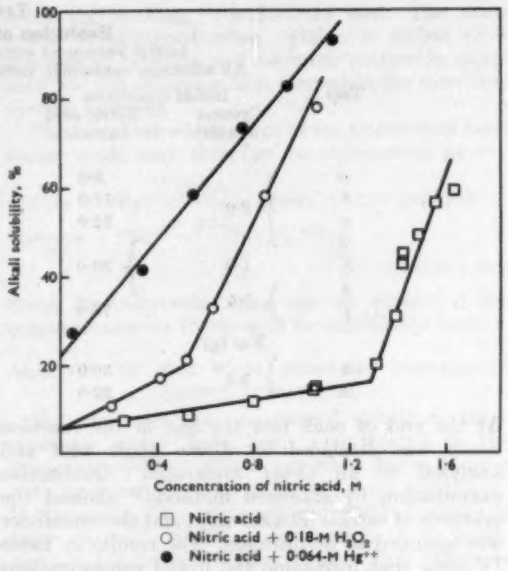


FIG. 5—Effect of initial reagent concentration (at 40°C) on alkali solubility of fur

carrotting solutions[17]. Other workers have concluded that the rupture of cystine bonds is the only essential reaction in carrotting[2, 8, 10].

The apparent necessity for reaction at two points calls to mind some similar conclusions concerning non-felting treatments[18], and it may be that carrotting is in fact a non-felting process applied selectively to the tips of the fibres. We have obtained improved felting rates by using several well-known non-felting treatments on the tips of rabbit fur fibres (though none of these were as effective as mercuric carrotting), but those non-felting processes which depend solely on surface modification did not produce any significant increase in felting rate when applied to the tips only, e.g. sulphuryl chloride in white spirit[19] and sodium hydroxide in butyl alcohol and white spirit[20].

A survey of the patent literature shows that very many attempts have been made, by empirical means, to improve on the traditional mercuric process. Although relatively high rates of felting have been achieved with some non-mercuric processes, none of these (as far as we are aware) produces a felt of a quality comparable with that from mercuric-carrotted fur, i.e. the overall degradation as measured by alkali solubility is always relatively smaller for mercuric-carrotted fur. We believe that the superiority of the mercuric process is due to the selectivity of the reactions between mercuric ions and keratin; attack at specific points in the protein molecule by relatively low concentrations of the reagent results in a *controlled* degradation of the peptide chains, i.e. fission of the main chain occurs more easily at those peptide bonds adjacent to the reaction sites. Other evidence supports this conclusion. Of the many amino acids combined with cystine in wool, serine is the most abundant[21]. Fission of peptide

bonds adjacent to cystine which has reacted with mercury should therefore cause an increase in the number of terminal serine residues; such an increase has been observed [10].

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[18] Alexander, Carter, and Earland, *J.S.D.C.*, **67**, 23 (1951).
[19] Hall, *ibid.*, **55**, 389 (1939).
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Notes

Bristol Symposium

The programme of lectures at the symposium on "Science and Craft in both Textile and non-Textile Coloration", to be held in the Grand Hotel, Bristol, on 20th–22nd September is as follows—

Wednesday 20th September

MORNING

Effect of heat-setting treatments on dyeing behaviour of nylon yarns and fabrics—*H. W. Peters and T. R. White* (*BNS*)

Dyeing polyacrylonitrile fibres with cationic dyes—*W. Beckmann* (*FBy*)

Interaction forces between polyacrylonitrile fibres and disperse and cationic dyes—*F. Feichtmayr and A. Würz* (*BASF*)

AFTERNOON

Coloration of plastics, with special reference to polyolefins—*C. Musgrave* (*Gy*)

Dyeing chrome-tanned leather with aid of ethylene oxide levelling agents—*J. Herndl* (*Ciba*)

Tuesday 21st September

MORNING

Modern physical techniques and colour formulation—*J. V. Alderson, E. Atherton, and A. N. Derbyshire* (*ICI*)

Control and specification of fluorescent whites and colours—*J. M. Adams* (*PATRA*)

Pigments, colour, and paint—*S. H. Bell* (*Paint Research Station*)

Practical problems in preparation and dyeing of cross-wound packages—*J. Whittaker* (*Robinson Bros., Blackburn*)

Friday 22nd September

MORNING

Application of vat colorants to Courtelle and blends with cellulosic fibres—*R. J. Hannay* (*ACC*) *and others* (*Courtaulds*)

A study of the diffusion of dyes in polymer films by a microdensitometric technique—*R. H. Peters, J. H. Petropoulos, and R. McGregor* (*MCST*)

Behaviour and significance in dyeing of abraded wool—*H. R. Hadfield and D. R. Lemin* (*ICI*)

Effect of dyeing and related processes on some physical characteristics of wool—*J. Elliott, N. Oldfield, C. B. Stevens, and C. S. Whewell* (*Leeds Univ.*)

AFTERNOON

Hydrolysis of reactive dyeings—*J. Benz* (*S*)

Details of the full programme, including social events, have already been circulated to members. Application forms should be returned to the Society as soon as possible.

Overseas Conference of The Textile Institute

The Textile Institute is holding a conference on "Crease-resistance and Crease-recovery" at Scheveningen, Holland, on 7th–12th September 1961. Ten papers will be given on 8th and 9th September, and there will be works visits on 11th and 12th September. Full details of the programme are given in recent issues of the Proceedings Section of *J. Textile Inst.*, and application forms are obtainable from The General Secretary, The Textile Institute, 10 Blackfriars Street, Manchester 3.

Association des Chimistes de l'Industrie Textile

The 34th Congress of A.C.I.T. will be held in Lyons, France, on 22nd–24th September. The following will present papers— M. Piganiol (Délégué Général à la Recherche Scientifique et Technique), Professor Champetier, M. Corbière (Rhodiaceta), M. Hureau (President, Silk Federation), M. Rey (Et. Gillet-Thaon), M. Niederhauser (CFMC), M. Jacquemart (Institut Textile de France), M. Mosnier (Ciba), and M. Jomain (CFMC).

There will be visits to mills, a reception at Lyons Town Hall, and a ball at Charbonnière Casino. Registration forms are available from the local committee— B.P.67— Lyon Terreaux.

Society of Leather Trades' Chemists

The Annual Conference of the Society will be held in the large Chemistry Lecture Theatre, Leeds University, on 22nd and 23rd September 1961. On

Friday morning there will be a discussion on "The Requirements of Leathers to Meet Modern Developments in Shoe Construction". Papers presented at the conference will deal with the chemistry of chrome tanning, correlation of colour tolerance determinations with average observer assessments, and application of polyurethane technology in leather manufacture. Programmes are obtainable from the Honorary Secretary, Forestal Land, Timber and Railways Co. Ltd., Technical Service Department, Ditton, Widnes, Lancashire.

Schweizerischer Verein der Chemiker-Coloristen

The S.V.C.C. is holding a conference on textile finishing (including crease-resist treatments, production of wash-and-wear fabrics, etc.) in Zürich on 11th–14th October. Twenty-eight papers will be presented. Details, programmes, and application forms are available from the Society's Offices or from Symposium SVCC, Postfach 142, Zürich 45.

Bradford Junior Branch

Certain of the details of the Bradford Junior Branch committee given in the July issue of the *Journal* (p. 284) were unfortunately incorrect. They should read as follows—

Chairman	E. N. Wood
Vice-chairman	C. T. Hardisty
Honorary Secretary	W. R. Hermes Jnr.
Assistant Secretary	V. L. Elsworth
Committee	G. Button
	A. Pickles

Report on the Work of the Patent Office

The 78th Annual Report of the Comptroller-General of Patents, Designs, and Trade Marks, shows there has been a further increase in the work carried out by the Patent Office. The number of applications and complete specifications filed is the highest ever received by the Office. The number of Patent Applications filed constitutes a new record of 44,914.

It is interesting to see, however, that there is a substantial increase in the number of specifications published— 31,260, compared with 19,450 in 1959. This shows that the efforts made to reduce the arrears have met with some success. The arrears of 37,068 unexamined complete specifications at the end of 1959 had dropped to 36,695 at the end of 1960 despite a filing of almost 2000 more complete specifications than in the previous year.

As regards the trend of invention in 1960, the Report shows that in the chemical field there was extended use of catalysts which determined the spatial arrangement of atoms in molecules, to polymerise monomers other than ethylene. In the textile field there was increased activity in the treatment of yarn to enhance its bulk and stretch properties, and interest was shown in the coating of prestretched transparent films which can be shrunk round frozen foods.

The statistics show that there was a substantial increase in the number of accepted complete specifications relating to apparatus for dyeing textiles. However, the number of specifications dealing with processes and materials for dyeing and otherwise treating textiles was slightly smaller. The number of applications from Japan, which in 1959 was greater than in 1958, showed a further increase in 1960. This may not be significant, since the number of applications from other countries, e.g. Switzerland, U.S.A., France, and Germany, increased similarly.

In the section of the Report dealing with Designs it is pointed out that there was a significant increase in the number of applications for designs for lace articles. There were 95 applications in the year, which was more than double the number received in 1959, and there was only one application for lace during the two years 1957 and 1958. Apparently, textile articles constituted the highest number of applications received. The total number of designs registered in 1960 was, however, smaller than in 1959.

The section dealing with Trade Marks shows that there was a substantial increase in applications received and also in Trade Marks registered, and it is stated that nearly all classes of goods contributed to the increase.

Finally, reference is made to the Bill introduced into the House of Lords to increase the period of grace for the payment of Patents and Designs renewal fees up to six months instead of three months as hitherto.

The Report can be obtained from the Stationery Office, price 1s. 6d. net.

L. E. Jones

Penguin Science Survey

The Penguin Science Survey is designed to give interested laymen information on recent developments in science and at the same time to provide scientists themselves with reviews of work in fields of study other than their own. These essays illustrate the growing interdependence of progress in different fields, and the increasing difficulty of dividing science into isolated and distinct subjects.

The first two volumes in the series have recently been published. Vol. 1 deals with the physical sciences and Vol. 2 with the biological sciences. Each volume costs 6s. The next issues will be published early in 1963.

Meetings of Council and Committees July

Council— 5th
Finance and General Purposes— 11th, 28th
Examinations Board— 14th, 15th, 28th
Colour Index Editorial Board— 17th
Publications— 18th
Diplomas— 28th

OBITUARY NOTICES

J. Holt

J. Holt, a Fellow of the Society and a member of the International Relations Committee, died in Bury General Hospital on 27th February at the age of 56. He was a student of the Manchester College of Technology and joined Geigy, then The Geigy Colour Company, in Dickenson Street, Manchester, as assistant in the Textile Laboratory in October 1921. When Geigy moved to National Buildings in the Parsonage he was in charge of the laboratory technical service. Early in the war, while remaining in charge of the laboratory, he took over the Supplies Department and so became responsible for the allocation of dyes under the stringent war-time regulations of the Government Dyestuffs Control. His success in this very difficult job was widely recognised. By the end of the war he had become Textile Sales Manager, and afterwards he was largely instrumental in the setting up of the Geigy area office in Belfast.

He always emphasised the importance of good relations with colleagues and business associates and his actions were guided by this principle. He was a keen member of the Manchester Rotary Club and in his earlier years he had been a cricketer of some note.

Jim Holt was held in high esteem by his many friends throughout the textile industry. He held a very special place also in the affections of his Swiss colleagues in Basle. In spite of poor health for many years past, which he bore with great courage, he never complained, and his sense of friendliness and humour endeared him to colleagues and customers alike. His flashing wit and repartee made him welcome in any company, and the sharper the exchanges the better he enjoyed them. His friends (and they are indeed many) will feel his loss deeply, and many younger people will remember gratefully the real and practical help he gave so freely.

F. R. Twemlow

The death occurred on 16th January, at the age of 71, of Francis Revill Twemlow, who for many years had been technical representative of Messrs. L. B. Holliday & Co. Ltd.

Twemlow's career in the dyestuff industry commenced in the technical application laboratory of the Berlin Aniline Co. Later he was employed by Levinstein & Co. Ltd., Manchester, where he gained experience in works and research laboratories. In October 1926 Twemlow joined the staff of L. B. Holliday & Co. Ltd., in the technical dyeing laboratory, and later became head of the Technical Department. As technical representative of L. B. Holliday & Co. Ltd. he was widely known and highly respected throughout the British Isles.

Francis Twemlow served on various technical committees of the Society, being a member of the Fastness Tests Co-ordinating and the Disperse Dyes Committees.

E. THORNTON

New Books and Publications

Titration in Non-aqueous Solvents

By A. H. Beckett and E. H. Tinley. Pp. iv + 56. 3rd Edition. Poole: British Drug Houses Ltd. 1960. No price.

The second edition (see J.S.D.C., **73** 427 (1957)) of this useful booklet has been increased in subject matter by about one quarter, such that almost the whole of the new material is included in sections dealing with practical applications. The number of references have been increased from 97 to 130, and at the end of the book are four tables of pharmaceutical substances assayed by non-aqueous titrations listing the solvents, titrants, and indicators used.

Some of the new matter includes, in the section on solvents, the use of acetic anhydride in absence of acetic acid for potentiometric titration of weak bases, and pyridine as a solvent for acidic substances. New titrants include trimethylbenzylammonium hydroxide and tributylamine in dioxan. The section on potentiometric titrations has been enlarged and there is a new section dealing with applications to synthetic organic chemistry.

The same excellent arrangement has been maintained, in that titrations of basic and acidic substances are dealt with separately, each taking into consideration appropriate solvents, indicators, titrants, and methods.

This booklet is a handy source of information for those new to the subject, and no doubt workers in this field who are already familiar with the previous edition will benefit from acquiring this one.

W. ARMFIELD

Walzengravur und Schablonenherstellung im Textildruck

By H.-G. Jakob and F. Weissgerber. Pp. ix + 339. Heidelberg: Melliand-Verlag. 1960. Price, DM 38.00.

This book consists of 339 pages, 226 of which describe roller engraving and 65 the preparation of screens.

The section on roller engraving begins with a brief historical review. This is followed by a description of the manufacture of the roller, its preparation for engraving, engraving processes (e.g. hand-, mill-, pantograph-, photogravure-engraving), etching, "touching-up", chromium plating, and the deposition of copper on rollers. The planning of an engraving department is described and details are given of the application of the roller to the mandril and of the handling and storage of rollers. The section dealing with preparation of screens also has a historical introduction. A description of screen materials follows, and methods

of application of material to the screen frame, of lacquer to the screen, and of the pattern are dealt with. Cleansing of the blank screen, screen storage, and planning of the screen-making department are also considered. The book ends with a literature survey, list and address index of suppliers, and a general index.

This book is very thorough; 110 pages are occupied in describing the many aspects of photogravure engraving. Omissions are very few, but no reference is made to the Briggs' roller-storage system or to the simultaneous engraving of rollers for Duplex printing. It would have been interesting if a chapter could have been included on the manufacture of roller screens for the Aljaba printing process. Localised chromium plating is a useful technique in roller repairing and might have been mentioned.

Even the expert will find much of interest in this publication, although it will not instruct him in how to mill-engrave a cross-over motif. The printing is clear and the book is of a handy pocket size. It can be recommended to all technicians with a working knowledge of the German language. F. FARRINGTON

Procion Dyestuffs in Textile Printing

Pp. 243. Manchester: Imperial Chemical Industries Ltd., Dyestuffs Division. 1960. No price.

The declared intention of this volume is to collate and present all the information currently available on the application of the Procion reactive dyes in textile printing. The eight chapters, each the responsibility of a named author, cover historical development and theoretical background, the printing of cellulosic fibres, viscose rayon tufted carpets, chlorinated wool and silk, the production of resist and discharge styles, printing behaviour, and fastness data. The theoretical section contains an abundance of quantitative data, presented graphically and in tables, with formulae as necessary, to support the conclusions set forth. The foreword expresses the hope that inclusion of this discussion of the basic principles governing the behaviour of the reactive dyes will assist in fuller understanding of the practical recommendations and also encourage users to experiment on their own account. Continuing rapid development in this field, of both new dyes and new procedures, means that any publication of this kind is inevitably incomplete, but the majority of recommendations have been substantiated in bulk working.

This volume is the latest in a long line of very useful monographs of a type which only the dyemaker can provide; like its predecessors it is very well produced. While there is no need to credit the dyemakers with completely altruistic motives in providing practitioners and students of our technology with such useful manuals, to fail to acknowledge gratefully their appearance would be ungracious indeed. C. B. STEVENS

Pigmente: Herstellung, Eigenschaften, Anwendung

Edited by H. Kittel. Pp. xii + 824. Stuttgart: Wissenschaftliche Verlagsgesellschaft m.b.H. 1960. Price, DM 178.

The chemical derivations of pigments are spread widely over both the inorganic and the organic fields. Inorganic pigments vary in the complexity of their production, from the crude "earths" and the ubiquitous iron oxides to highly refined artist's colours, while organic pigments can be found to illustrate almost every one of the known chromophores and to provide analogues or derivatives of almost every class of dyes. Further, the physical properties of pigments, in part intrinsic and in part controlled in manufacture, are critical for each of the highly varied protective or decorative purposes for which pigments are used. It is not surprising therefore that there have been few really comprehensive treatises on pigments and their applications. One of the best known, but for some time out of date, the *Körperfarbe* of Hans Wagner, has been rewritten and issued under the above title, being now the work of an editor and twelve specialist co-authors.

The scope of the book and the balance of interests can be broadly gauged from the pages devoted to the main themes—optical, chemical, and physical bases of pigments (130 pp.), basic processes of manufacture (14), properties of inorganic pigments (259), properties of organic pigments (57), colour lakes (40), techniques involved in preparing pigments for use (mixing, dispersing, use of substrates) (91), the composition, properties, and requirements of the various coloured systems into which pigments enter, with selections of suitable pigments (110), testing and methods of investigation (38), tables, literature references, and indexes (75). Thus a large proportion of the work is devoted to discussion of the underlying chemical and physical bases of the pigments themselves, the complex systems with which they must be embodied in order to produce technologically useful colouring compositions, and the other components of those systems, e.g. oils, resins, and solvents, with which the pigments must be compatible. All this is done systematically, clearly, and thoroughly, and will probably be viewed by many as the most valuable feature of a valuable work. This is a book which anyone concerned with investigations or research on pigments would be glad to have at his elbow, and it is unfortunate that the high price (about £16 at present values) must seriously limit its availability.

There are some points which call for criticism in a work which aims to be regarded as a standard text book. In the descriptions of the properties of pigments, individual organic pigments are generally treated in less detail than are inorganic pigments. For example, the brief treatment of the phthalocyanine pigments does less than justice to this scientifically and technologically important group, and the inclusion of more of the known chemical constitutions of individual azo pigments, particularly the constitutions of those pigments illustrated in the patterns bound into the book, would

have increased the value of the book for students. Again it is a drawback that the commercial names of pigments used in the text are almost completely confined to those of manufacturers in Western Germany, although many of the pigments in question are manufactured by numerous firms in every industrial country in the world. Mention of all the names used could not be expected, but quotation of the *Colour Index* Generic Names would have overcome the difficulty and assisted many users of the book. In contrast it must be recorded that the numerous references, collected in an appendix of 40 pages, are widely drawn.

M. LAPWORTH

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

Ciba Ltd.

CATALYSER RB— This is a liquid, water-soluble catalyst for use in producing Phobotex FT and FTS water-repellent finishes. By its use the preparation of Phobotex emulsions is simplified since only one product is required and this can be added in undiluted form.

UVITEX ERN— This 31-page booklet describes a new fluorescent brightening agent primarily intended for use on polyester fibres on which it gives slightly reddish whites of outstanding fastness to light. It is also of interest on secondary cellulose acetate, triacetate, polyamides and polyvinyl chloride fibres and on mixtures of these with cotton and wool. Full application details and fastness data are given and patterns are included.

Farbenfabriken Bayer A.G.

GREY SHADES WITH INDANTHREN DYESTUFFS ON COTTON PIECE GOODS (PIGMENT PADDING PROCESS)— This card contains dyeings on cotton twill of 18 different vat dye combinations, each in 6 depths. They have been produced by pigment padding followed by jig development. The main components are Indanthren Greys EGR and EBN. The latter is particularly recommended for pale to medium depth colours because of its very good levelling and migrating power.

LEVAPON NSW— This is a non-ionic scouring agent for all types of fibres. A particular advantage is that full detergent power is developed in acid solution. It is thus of interest for washing wool goods dyed with level-dyeing acid dyes when there would be danger of dye bleeding in neutral or alkaline solutions.

MESITOL WLS— This product is intended to reduce the uptake of direct dyes by wool when dyeing wool–cotton mixtures. It is particularly effective in acid dyebaths, offering considerable advantages over the previous combination, Mesitol WL and Avolan IL. The new product can be used alone since it also exerts a levelling action. Only when 2:1 dye:metal complex dyes are used for the wool or where additional levelling is required for the direct dye is addition of Avolan IL recommended.

PERLIT SI; PERLIT SIH— Perlit SI is a silicone-based water-repellent agent intended for use on synthetic fibres, wool and silk. Used alone, it does not give optimum results, and Perlit SIH, a self-solution of a polysiloxane, must also be incorporated in the impregnating liquor to cross-link or set the silicone.

ASTRAZON BLACK WRL— This cationic dye gives full blacks of good fastness on acrylic fibres, and it is recommended that staple fibre materials be dyed at 98–100°C and continuous-filament yarn in packages at 120–125°C. It is very suitable for use on mixtures of acrylic fibres and wool or cellulosic fibres since after dyeing for the recommended time at 96–98°C the latter are virtually unstained and no special cleaning treatment is required. Fastness figures on Dralon (new) include— light (daylight) 6, washing (b 60°C) 4–5, severe milling 4–5.

DYEINGS ON DRALON (NEW)/CUPRAMA MIXTURE YARN— This card contains 20 solid dyeings on this particular acrylic fibre/cellulosic fibre mixture. The acrylic fibre is dyed first at the boil using cationic dyes at 96–98°C, the material then given a short rinse and the Cuprama dyed at 75–85°C in a fresh bath with selected fast-to-light direct dyes. The dyeing characteristics of Dralon (new) make it unnecessary to give an intermediate scour since practically no staining of the cellulosic fibre occurs if the recommended time and temperature (96–98°C) of dyeing are adhered to.

Geigy Co. Ltd.

IRGASOL SW— This provisional circular describes a new product primarily intended for promoting level-dyeing when applying 2:1 metal-complex dyes and aggregated acid wool dyes to wool. It is mainly non-ionic in character and by adding increasing amounts from 0·5% to 3% (on wt. of material) the pH of the dyebath can be reduced from 6 to 4 and at the same time an even higher standard of levelness may be obtained. The product is specifically recommended for dyeing yarn in hank form, cloth, including carbonised material, felt hoods and garments. It is also of value as a dyebath additive when dyeing all but a few of the Eriochrome range of chrome dyes. As is now appreciated, with Irgasol SW as with similar powerfully surface-active compounds, addition of an anti-foaming agent, in this instance Irgafoamal SE, is strongly advised to improve liquor flow in circulating-liquor machines and floating of cloth in winches.

IRGAFOAMAL SE— This is a highly dispersible o/w emulsion of a silicone which is a highly effective anti-foaming agent, the concentration required being 10–200 p.p.m. Its effect is not restricted to the surface of dye liquors but promotes the escape of air trapped in fibre masses. It is of great value in preventing development of the foam which otherwise is produced when non-ionic and weakly cationic compounds are present in dyebaths.

Imperial Chemical Industries Ltd.

TECHNICAL INFORMATION LEAFLETS—

Dyehouse No. 594 (Replaces No. 559). Viscose Rayon: The Warm (Bicarbonate) Batchwise Dyeing Process for Procion Dyestuffs— It has been established that if cold-dyeing Procion dyes are applied to viscose rayon at 50–60°C at pH 7·5–8·5 two important advantages result. Firstly, maximum colour yield in full depths is obtained with certain dyes, particularly those which tend to aggregate in cold solutions. Secondly, much better penetration results and better-quality dyeings are obtained in all depths. These considerations are particularly important when processing spun rayon cloth and yarn packages. Details of dyeing methods are given and the cold-dyeing Procion dyes are classified according to the colour value obtained by this method in comparison with the normal process.

Dyehouse No. 596 (Replaces Nos. 349, 415 and 468). Dyeing of Terylene Polyester Fibre: One-bath Azoic Process for Navy Blue and Black Shades on Loose Staple, Slubbing and Yarn— Details are given for producing navies with Brentamine Fast Blue B Base and Brenthol FO and blacks with Dispersol Diazo Black B and Brentosyn OT by a one-bath method at 130°C. Advantages claimed over the two-bath method include— considerably shorter dyeing time, economies in dyes and auxiliaries, dyeings of good rubbing fastness produced more easily, and (in case of blacks) superior light fastness. An alternative dyeing method for blacks is offered where there is any risk of settling of the Brentosyn OT in the reserve tank from which it is added to the dye vessel.

Dyehouse No. 597. Colour Instability in Pale-shade Air-drying Paints— Four red organic pigments have been found to be unstable in pale-colour decorative paints,

severe loss of tinctorial strength occurring on drying. The ratio of coloured pigment to opaque white pigment at which this effect has been observed is less than 1:100.

Dyehouse No. 598. Inks— Writing (Fountain Pen), Ball Pen, Drawing, Stamp Pad, etc.— This nine-page note gives information on typical formulations and the dyes used for the most important of them.

Dyehouse No. 599. Use of Anti-foaming Agents as an Aid to the Production of Level Dyeings— The use of Silcolapse 437 as an anti-foaming agent is described. It has been shown (see Hadfield and Lemin, J.S.D.C., **77**, 198 (1961)) that foam from residual detergents, certain dyes, and many auxiliary products can produce unlevel dyeings owing to dye liquor failing to circulate uniformly through the material. Silicone anti-foaming agents, e.g. Silcolapse 437, can cure the trouble. It is essential that the anti-foaming agent is added as early as possible in the process. It is much less effective in destroying foam already formed. Quantitative data showing the effect on liquor flow of adding 50 p.p.m. of Silcolapse 437 are given.

Dyehouse No. 601 (Replaces Nos. 442 and 529). Wet-fastness Properties of Procion Dyeings— The presence in a dyeing of dye not chemically combined with the fibre is due either to incomplete removal of such dye during soaping subsequent to dyeing or its production by splitting of the dye–fibre bond on storage. The amount of loose dye formed by such breakdown is small and is virtually insignificant with most cold-dyeing Procion dyes and all the "H" dyes. Addition of ethylenediamine to the soaping liquor and of Fixanol PN to the last hot rinse after soaping will produce the maximum wet fastness obtainable with cold-dyeing dyes.

Dyehouse No. 603. The Procion–Resin Process for Cotton Fabrics: Factors Governing Textile Properties— Information is provided on the effect of such variables as temperature of curing, amount of resin, and type of catalyst and auxiliaries used on the behaviour of the treated material in finishing and the characteristics of the finished cloth.

Dyehouse No. 604 (Replaces No. 208). Colours for Phenol–Formaldehyde Moulding Powders— A list of suitable colours is given together with fastness figures for stability to heat, bleeding in water, soap solution, ethanol and amyl acetate, and fastness to light.

Dyehouse No. 605 (Replaces No. 240). Pigments for Urea–Formaldehyde Moulding Powders— Lists of pigments suitable for colouring both α-cellulose-filled and wood-filled urea–formaldehyde mouldings, together with data on fastness to light, heat, water and ethanol.

Dyehouse No. 606 (Replaces No. 192). Pad–Jig and Pad–Winch Application of Direct Dyes to Spun Viscose Rayon Piece Goods— The information in this note is complementary to that given in *Continuous Dyeing by Pad–Steam Techniques*. Pad–jig and pad–winch processes merit consideration because their use renders extensive alterations and additions to existing plant unnecessary and the use of the more specialised pad–steam equipment is avoided. Practical application details are given and padding conditions discussed.

Dyehouse No. 607. Wool: Effect of Dispersol CWL on Level-dyeing Acid Dyes— In addition to its use in promoting level dyeing when using fast-to-milling acid and chrome dyes (A.P.L. No. 131 and T.I. (Dyehouse) No. 595), Dispersol CWL has been found to promote level-dyeing with certain (mainly monosulphonated) equalising acid dyes. The use of 1–2% of this product produces a considerable retarding effect without any significant effect on final dyebath exhaustion. It has also been found to reduce skittery dyeing behaviour with consequent increase in colour yield and to assist in the production of level dyeings on cloth the surface of which has been locally damaged by abrasion.

Dyehouse No. 608 (Replaces Nos. 248, 264, 297/8, 327, 339 and 355). Alcian "X" Dyestuffs in Textile Printing: A Tabular Survey— This note contains a shortened version of the technical information contained in the pattern card *Alcian "X" Dyestuffs in Textile Printing* and also an emulsion thickening recipe established since the card was issued.

Dyehouse No. 609. Paper Industry: Colour Index Numbers of Dyestuffs Offered— Part I numbers are given for these. C.I. numbers of the Edicol range of food dyes are also given in view of recent legislation in a number of countries relating to the use of additives in food-packaging materials.

Dyehouse No. 610. Paper Dyeing: Effect of pH— The effect of pH on the dyeing behaviour of basic, acid and direct dyes and also pigments is tabulated together with the optimum pH range. It is noted that fixing agents such as Tanimol WR and Lissatan AC (with basic dyes) and Fixanol PN (with acid dyes and pigments) help to promote uniformity of coloration by widening the pH range over which dye strength is maintained.

Dyehouse No. 611. Paper Coating: Perminal KB— Perminal KB is recommended as a more convenient alternative to pine oil as an anti-foam in alkaline paper coating mixes.

Dyehouse No. 612. Paper Dyeing: Two-sidedness— Structural two-sidedness, caused by preferential deposition of fine particles on the top side of the paper, inevitably leads to colour two-sidedness. General recommendations for reducing this fault to a minimum are given for both filled and unfilled papers.

Dyehouse No. 612. Solubility of Paper Dyestuffs— The solubilities of a range of paper dyes in Manchester water (Hardness 3° Clark) at 25°C and 80°C are tabulated.

Dyehouse No. 614. Paper: Lissatan AC for Bewoid Sizes— Lissatan AC is recommended as an additional stabiliser for casein-stabilised, fluid paper-making sizes of high solids content and consisting almost entirely of free or unsaponified rosin (Bewoid sizes).

Dyehouse No. 615. The Washing of Coloured Work with Lissapol NK and Fixanol PN— The process consists essentially in treating the goods in a solution of a cationic agent (Fixanol PN) in presence of a non-ionic detergent (Lissapol NK) under neutral or weakly acid conditions for 5 min at 100–130°F. The cationic agent "fixes" direct dyes present which would otherwise tend to mark-off. Alkali is then added as required and washing continued in the normal way. It is suggested that mixed coloured work can be safely processed as one large load by this method. Yellow dusters must still be excluded.

Dyehouse No. 616 (Replaces No. 504) Lissapol GLN in the "Poensgen Contra-flow Carousel" Washing Machine— An improved method is described in which Lissapol GLN and alkali are used without the need to "stabilise" the mixture with Calsolene Oil H8.

Dyehouse No. 618. Procion Dyestuffs: Application to Wool/Viscose Union Piece Goods by the Warm (Bicarbonate) Method— This method, previously recommended for viscose rayon, has been extended to blends of this fibre with wool for producing medium- to full-depth dyeings. It is not recommended for pale dyeings or most contrast effects, or for wool/cotton mixtures or blends containing modified (damaged) wool. Dyeing at 50–60°C in presence of sodium bicarbonate has been shown to have no significant effect on the tensile strength of virgin wool.

Brenthol and Brentamine Combinations on Cotton and Viscose Rayon— This card contains dyeings in a single depth on unmercerised, bleached cotton cloth and filament viscose satin of 71 azoic combinations. They cover a wide range of colour and have good fastness to light and wet treatments. Brenthols of both high and low substantivity have been used in order to meet the different requirements of the various bulk-processing methods. A general procedure for applying them is described with special notes on the dyeing of viscose rayon and cotton/viscose rayon mixtures, the use of standing baths and combinations of Brenthols.

Acid Dyestuffs for Wool: Vol. 2. Acid Milling Dyes— This card contains dyeings in four depths on wool cloth of 54 dyes including 15 Carbolan and 34 Coomassie dyes, together with 5 Solway dyes which have been included in this section on the basis of their colour and dyeing behaviour.

Sandoz Products Ltd.

Artisil Scarlet 3GFL; Foron Scarlet 3GFL— This disperse dye gives yellowish scarlets on secondary cellulose acetate, triacetate, Terylene and Courtelle. Fastness figures on Terylene include— light 7, pleating (Test 2) 5, washing (S.D.C. Mechanical Test A) 5.

Foron Blue BL— This disperse dye gives bright blues on Terylene, for which it is particularly suitable, alone and

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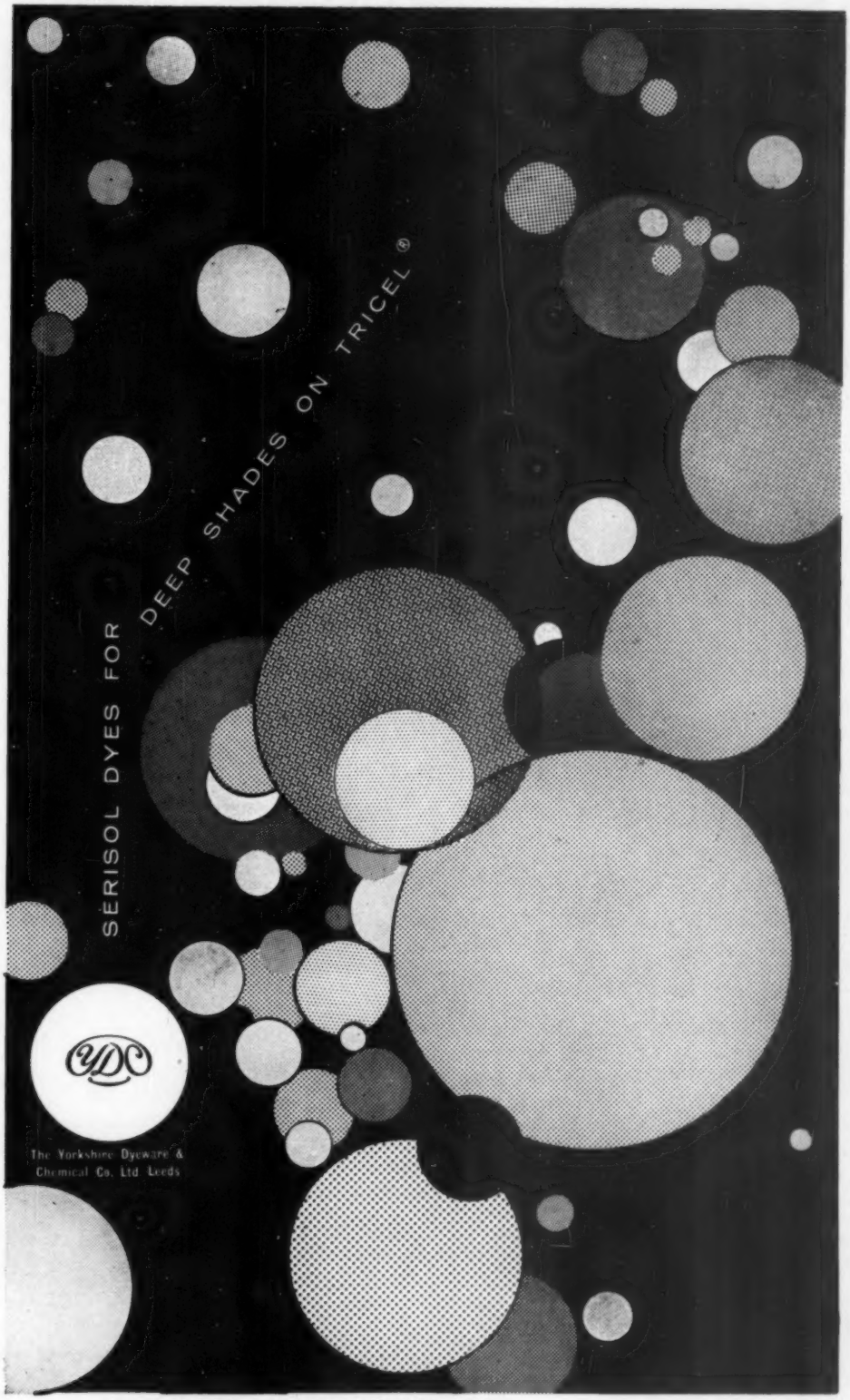

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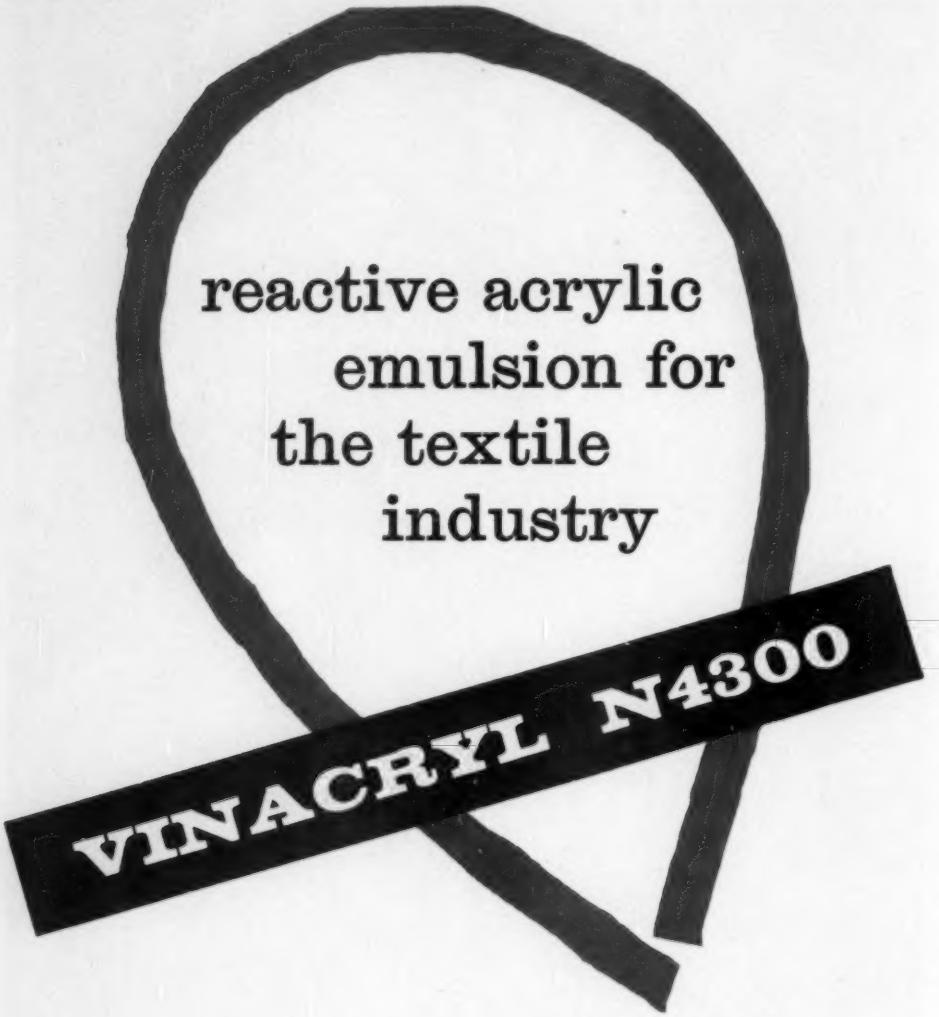

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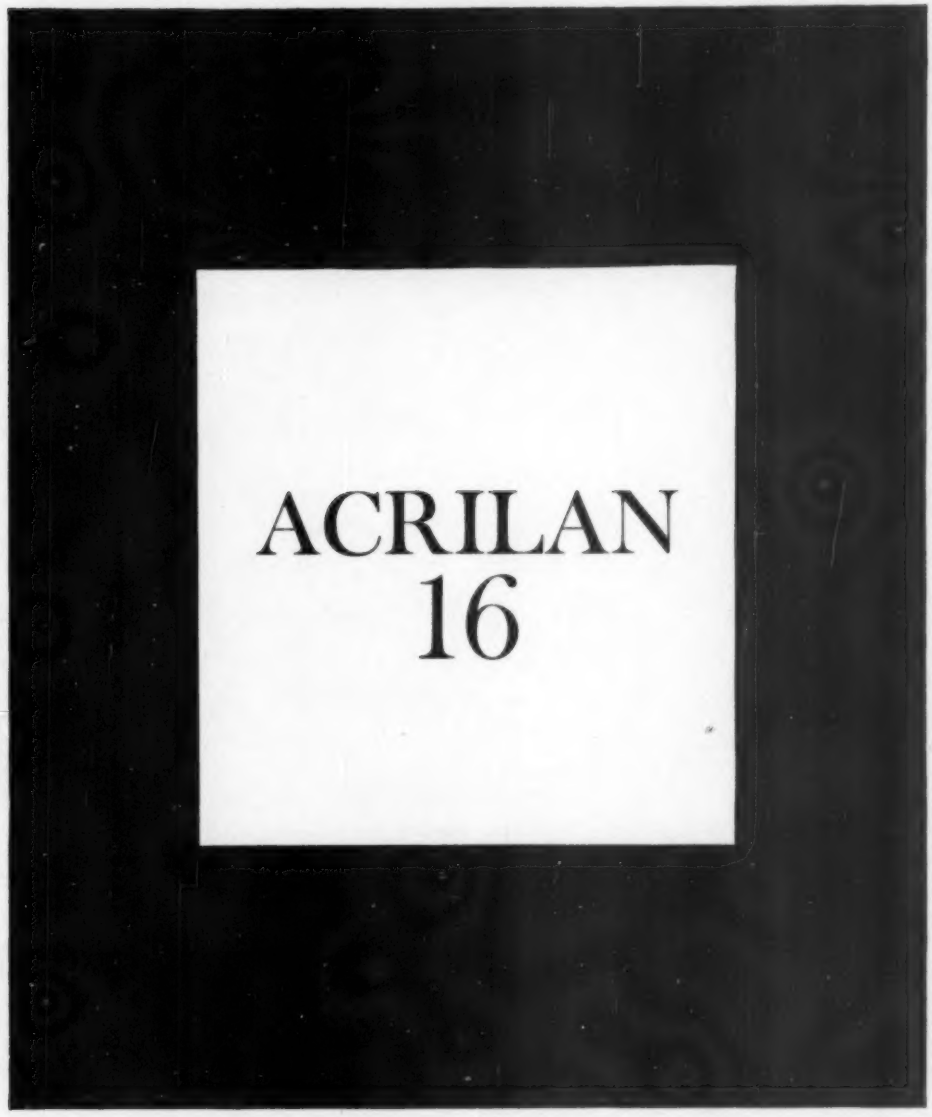

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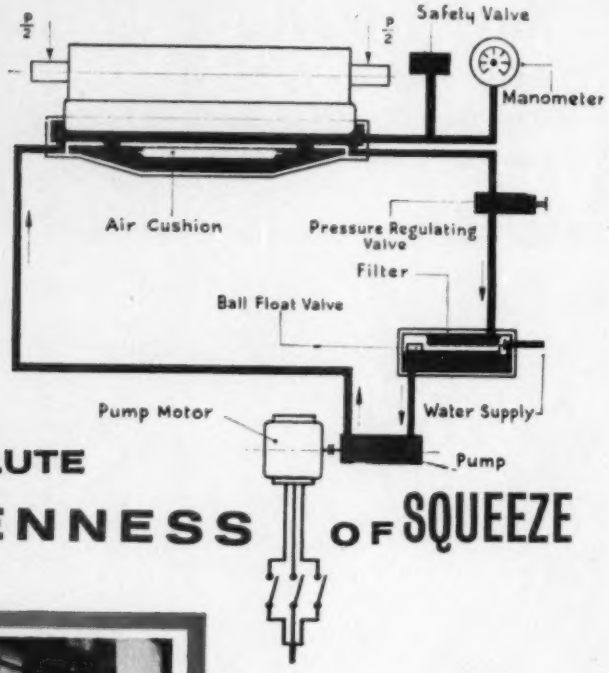

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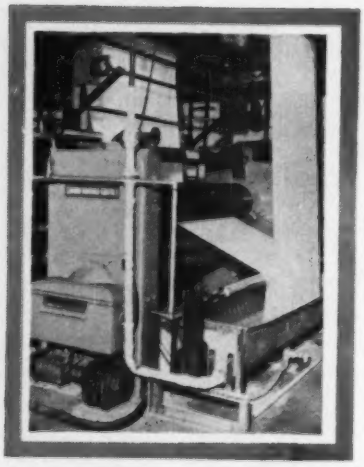

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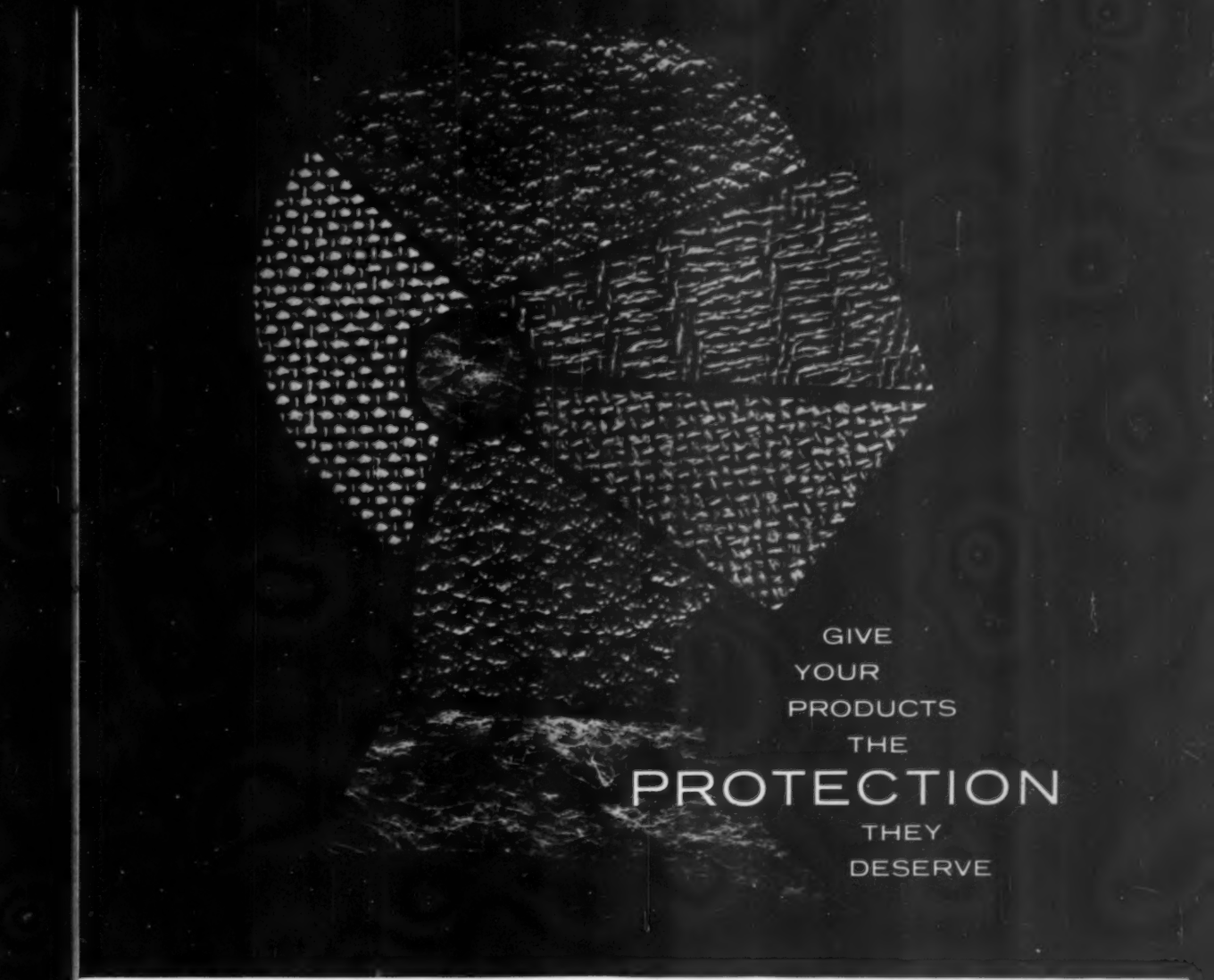

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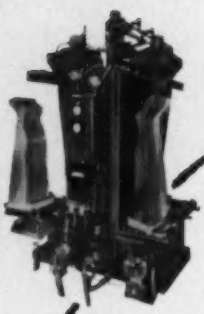

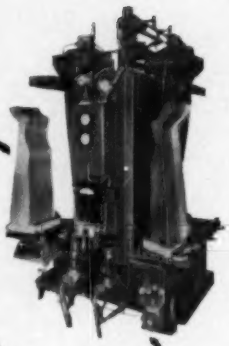

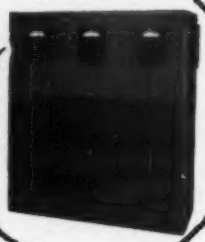

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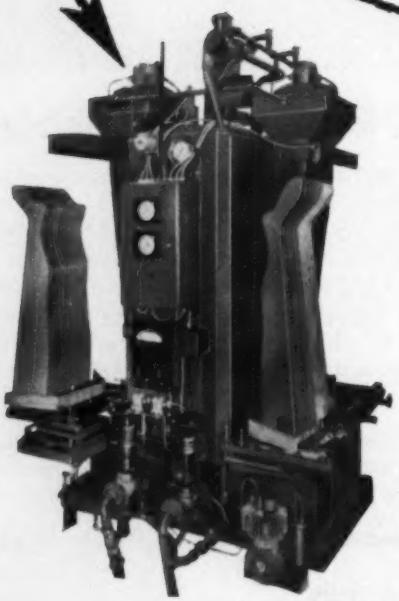

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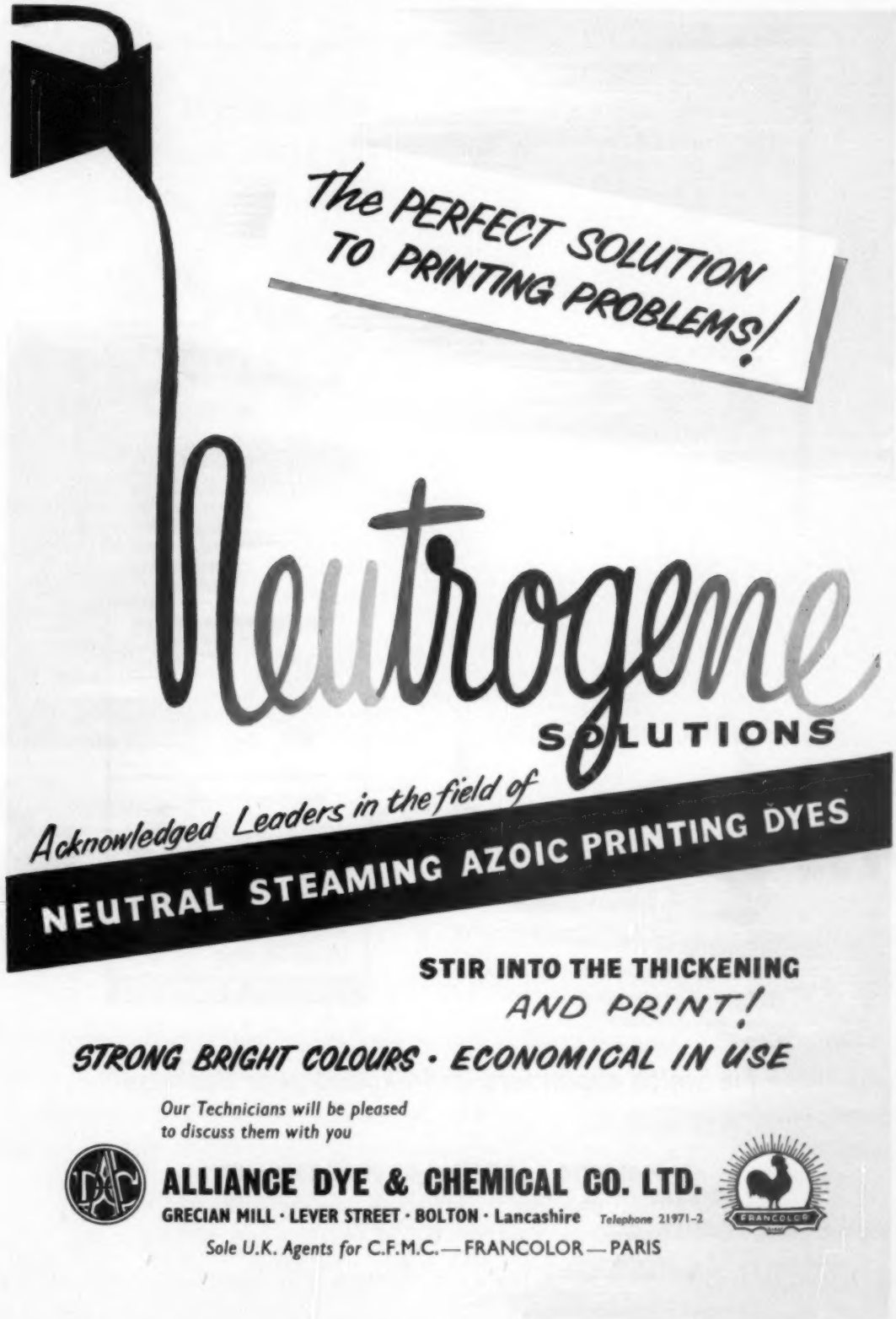
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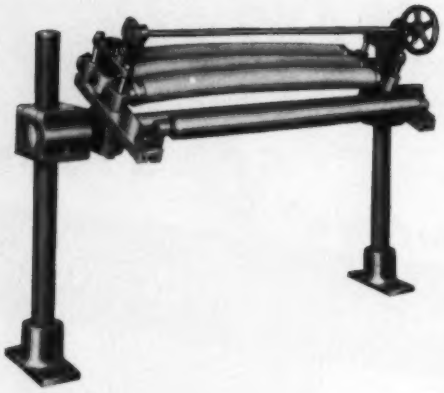

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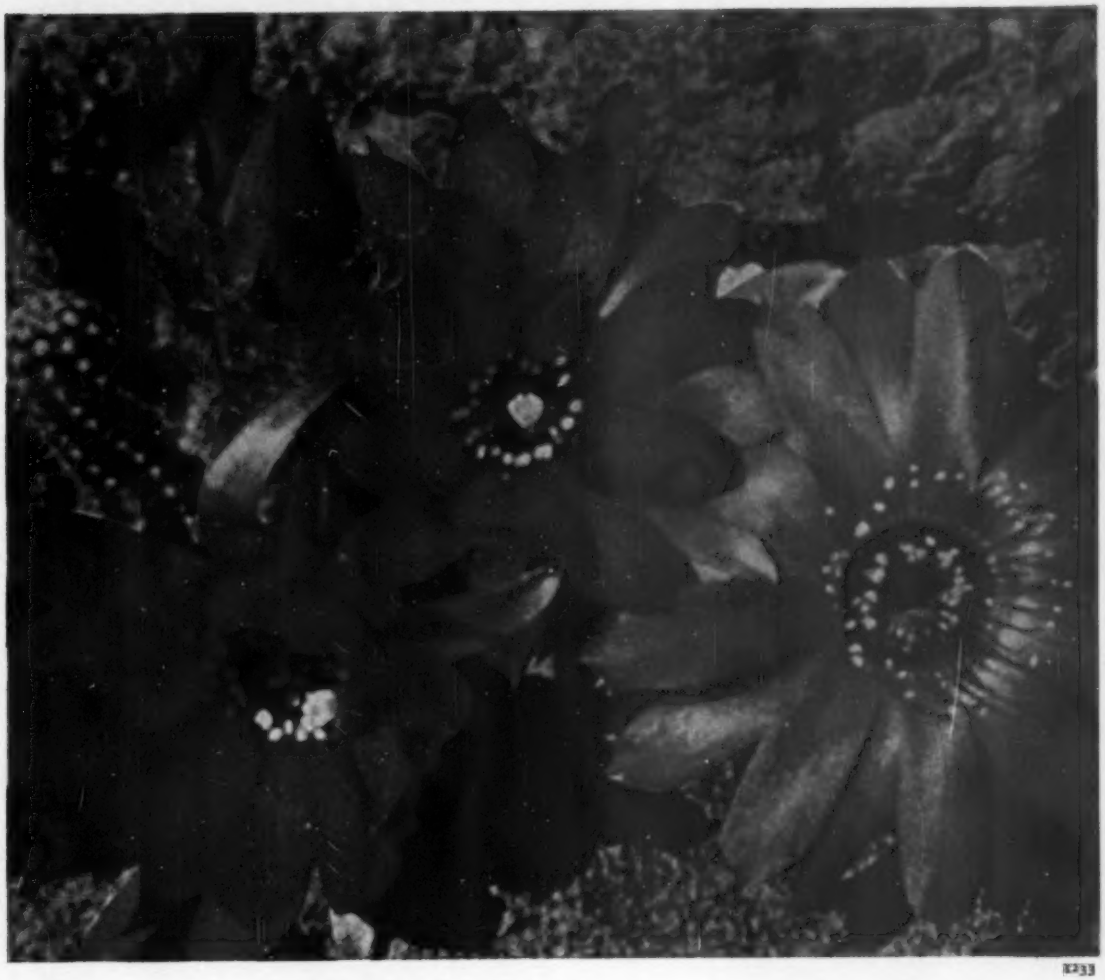

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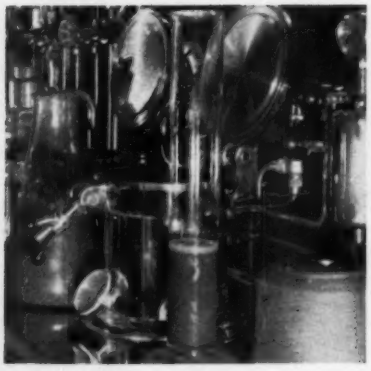

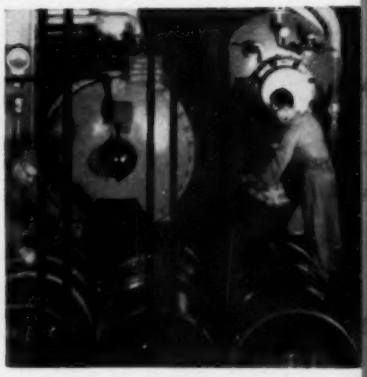

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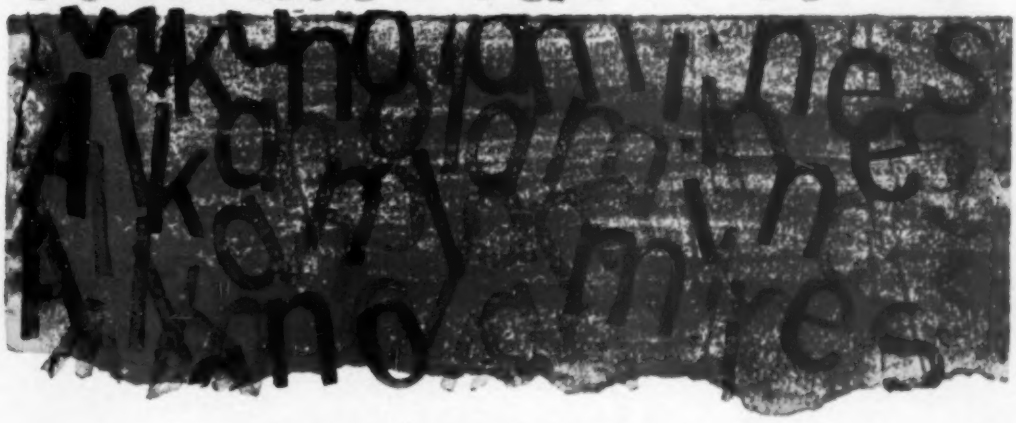

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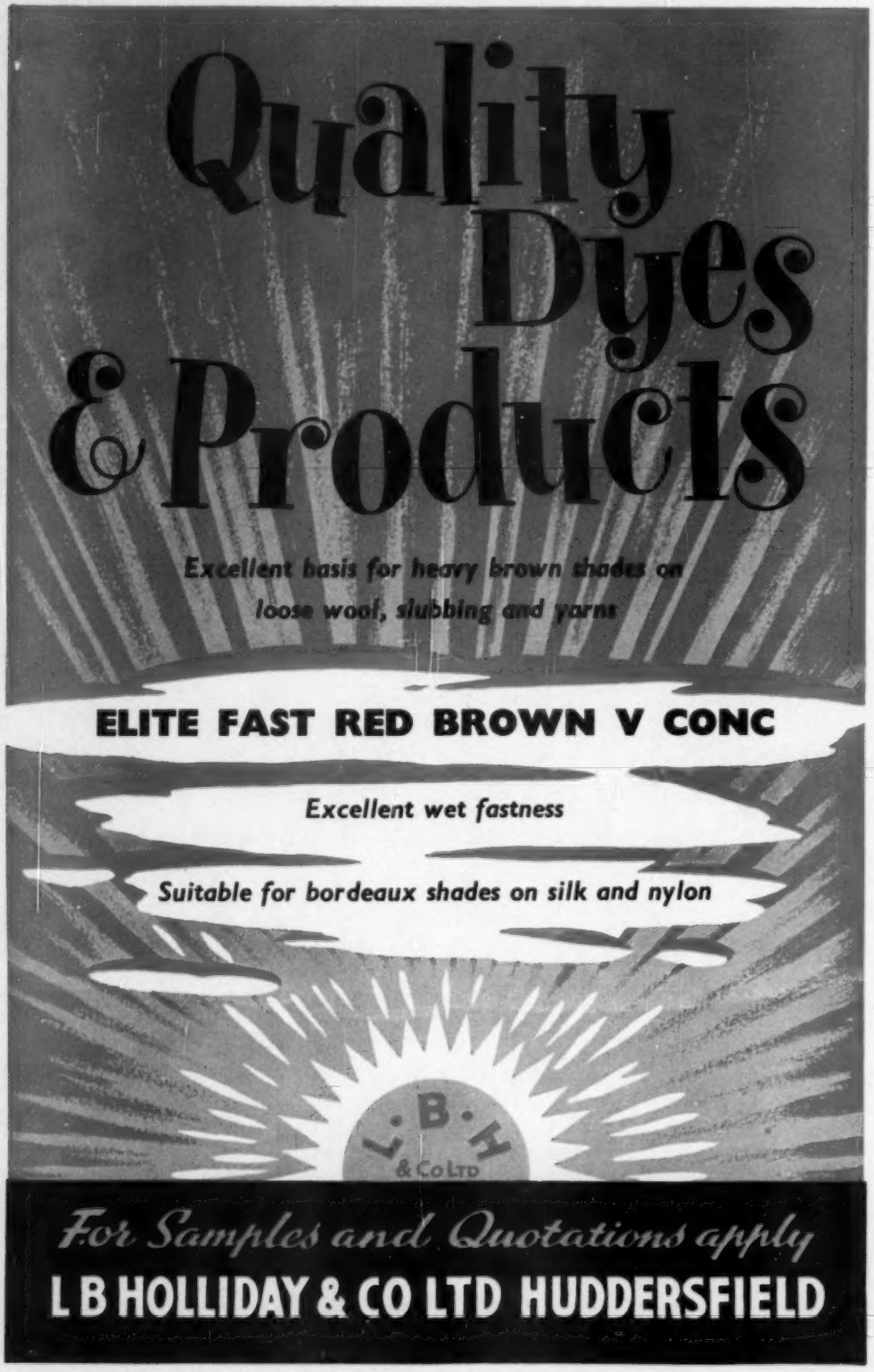
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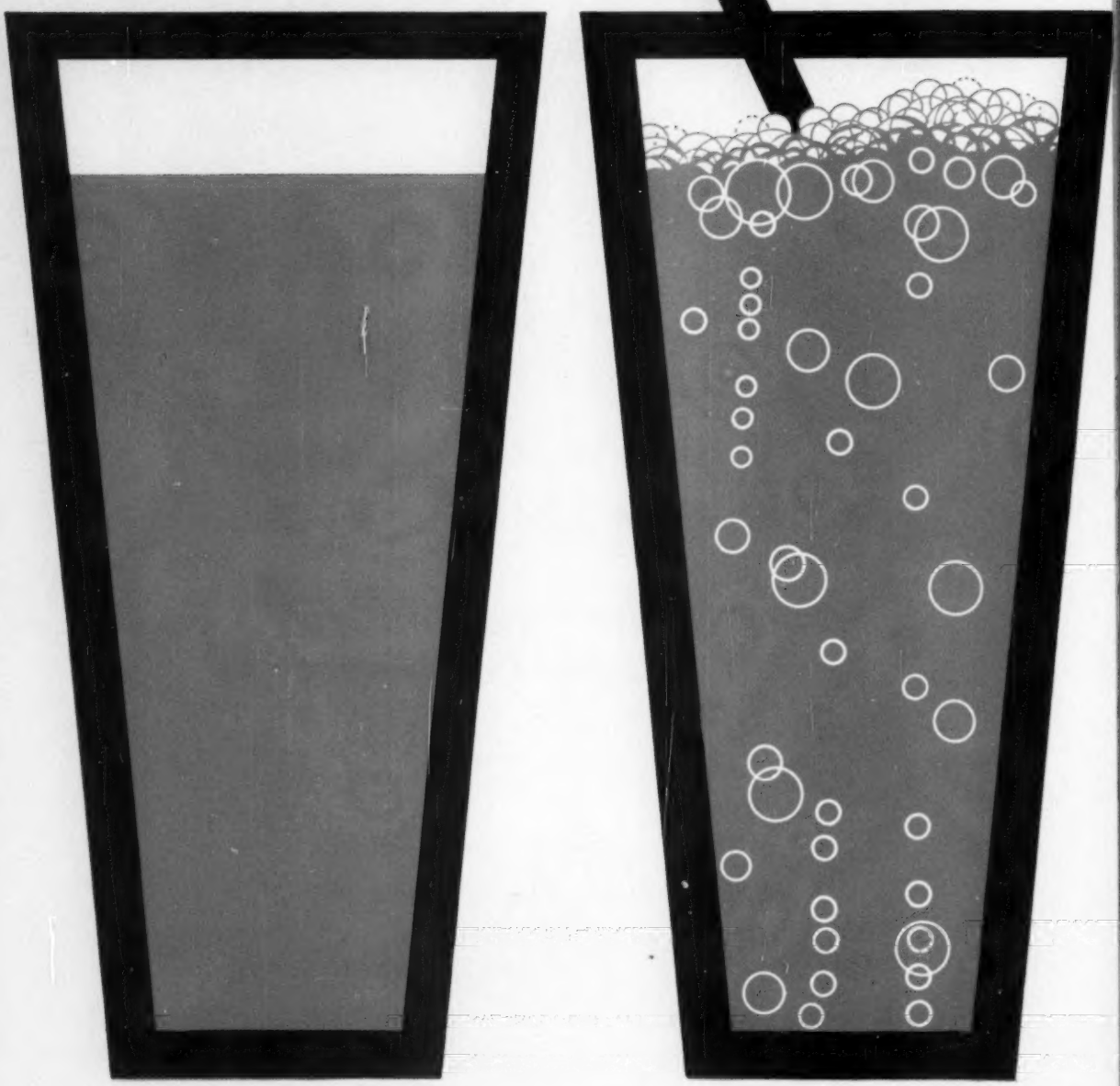

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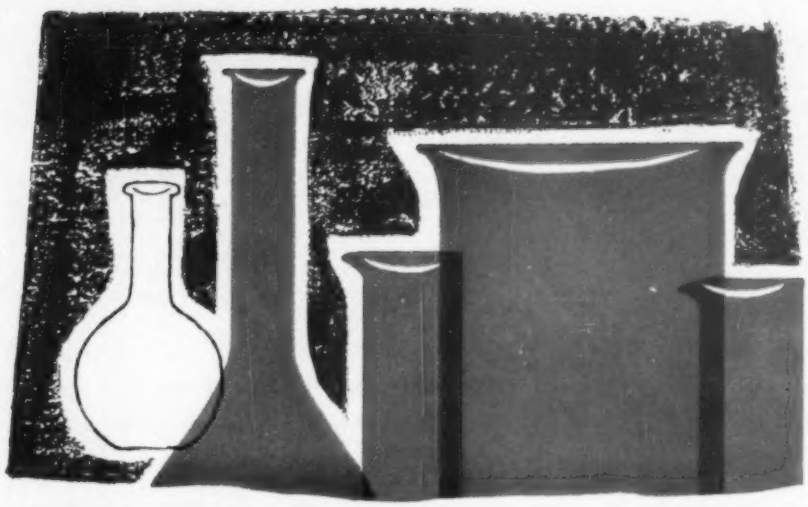

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Procion Brilliant Orange 2R
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in mixtures with Foron Scarlet 3GFL and Yellow RGFL. A selection of mixture dyeings on Terylene slubbing dyed with these dyes using Dilatin DB as carrier is included. Foron Blue BL is also of interest on secondary cellulose acetate, polyamides and triacetate. Fastness figures on Terylene include— light 6–7, sublimation (Test 2) 4–5, washing (S.D.C. Mechanical Washing A) 5.

Solar Scarlet 2GL— This direct dye gives bright yellowish scarlets on cellulosic fibres. The fastness to light of dyeings is good and is still further improved slightly when crease-resist-treated with urea–formaldehyde. Fastness figures include— light 5–6, handwashing 3, perspiration 3.

Sandoz A.G.

Artisil Red RL; Foron Brilliant Red RL— This disperse dye gives bright bluish reds on secondary cellulose acetate, triacetate, polyester fibres, polyamide fibres and Acrilan. It may be applied by both carrier and high-temperature methods to give dyeings of good fastness to light. Wet fastness on triacetate, polyester fibres and Acrilan is also good. Fastness figures on Dacron include— light (daylight) 7–8, alkaline milling (40°C SNY) 4–5 (staining of wool), pleating (1 min 220°C) 1 (staining of Dacron).

Drimarene Golden Yellow Y–R; Z–R— These two reactive dyes give bright golden yellows on cellulosic materials. Golden Yellow Y–R is intended for pad-dyeing and the Z–R brand for printing. Fastness figures on mercerised cotton include—

	Light (Daylight)	Washing (95°C)	Hypochlorite (ECE mild)
Golden Yellow Z–R	5	4–5	1
Golden Yellow Y–R	5	5	1

Drimarene Yellow Z–5GL; Yellow Y–5GL— The two reactive dyes give bright, pure yellows on cellulosic fibres. Yellow Z–5GL is intended for pad-dyeing and the Y–5GL brand for printing. They replace the corresponding 4GL brands. They are of outstanding stability in padding liquors and printing pastes. Uncombined dye is readily removed by washing. Dyeings and prints are stable to crease-resist finishing and dischargeable to white. Fastness figures on cotton include—

	Light (Daylight)	Washing (95°C)	Hypochlorite (ECE mild)
Yellow Z–5GL	6–7	4–5	1
Yellow Y–5GL	6–7	5	1

Palette, Jubilee Number 1886–1961— This issue contains four essays, ranging from the scientific to art, philosophy and theology. "Colour in Life" and "The Liberation of Colour" are particularly interesting, illustrated as they are by some very fine coloured reproductions of photographs of natural objects and paintings.

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I— PLANT; MACHINERY; BUILDINGS

Washing Pigments in a Fluidised Bed

T. Blickle and P. Kaldi

Chem. Tech. (Berlin), **12** (1960) 521–524
Chem. Abs., **55** (17 Apr 1961) 6955

Equations for the washing of pigments in a fluidised bed have been developed and their applicability tested for red and yellow iron oxides (C.I. 77491 and 77499), green chromium oxide (C.I. 77288) and lead chromate (C.I. 77600). As a result purer products were obtained with less consumption of water, and the plant takes up much less space than that hitherto used. C.O.C.

PATENTS

Laboratory Dyeing Machine

Ciba *BP* 863,608 (Switzerland 7 Apr 1956)

Several dyeing vessels, e.g. metal beakers, are placed in a heating bath. The vessels stand directly on the bottom of the bath, the bottom itself being the heating means.

BP 863,609 (Switzerland 7 Apr 1956)

Apparatus for holding the specimens to be dyed comprises a vertical rod and a flat spiral member fixed at its inner end to one end of the rod and forming a sharp point at its outer end.

BP 863,610 (Switzerland 7 Apr 1956)

The specimen holder comprises a vertical rod and < 5 prongs, each prong being fixed at its inner end to the lower end of the rod to radiate horizontally therefrom and having its outer end turned up to hold a test-piece. C.O.C.

Yarn Dyeing Machine

Obermaier & Cie *USP* 2,944,318 (28 Jan 1958)

Machine incorporating a device for adjusting the distance between the upper and lower rods holding the yarn as the yarn shrinks during dyeing. C.O.C.

Doctors for Roller-printing Machines

Gillet-Thaon, Ets. Gillet & Fils, et Blanchisserie & Teinturerie de Thaon

BP 863,426 (France 16 July 1958)

A tube of flexible material which is filled with air or other fluid under pressure is placed parallel to the roller and between the doctor blade and an associated rigid element also placed parallel to the roller and fixed transversely to it. The tube is of such a size that when pressure is applied to it it presses against both the doctor and the rigid element. This enables the doctor device to be of reduced size and to exert even pressure on the roller along the length of the doctor blade. C.O.C.

Doctor for Use with a Hot Roller

Bird Machine Co. *BP* 869,246 (U.S.A. 18 Aug 1958)

Describes a doctor blade support which is extremely resistant to warping upon substantial changes in temperature. C.O.C.

Wet Treatment of Textiles

J. T. Cerda *BP* 863,619 (Spain 17 Aug 1956)

The material to be treated is wrapped in several layers around the perforated peripheral surface of a drum which rotates in a closed vessel containing the processing liquor. The interior of the drum is in direct communication with the vessel through an opening in an end of the drum, which opening is at least in part below the level of the liquor. The rapid rotation of the drum forces the liquor into the drum and then through the material wrapped around the drum back into the vessel. C.O.C.

Open-width Wet or Gaseous Treatment of Textiles

E. Küsters *BP* 863,773 (Germany 16 Oct 1958)

Two conveyors, a lower and an upper one, move through the treating medium. The textile is placed in folds on the lower conveyor, the depth of the folds being more than the distance between the conveyors so that the material is securely held between the conveyors so that the folds are not disturbed. The path of the conveyor is at first obliquely downwards and is then reversed to reverse the sides of the folds before they are drawn off the lower conveyor. It is preferable that the distance between the conveyors gradually diminishes between the point where they first become associated and the point at which their paths diverge. C.O.C.

Treating Textiles in Rope Form

BrC *BP* 864,092 (13 Nov 1956)

A machine suitable for processing a wide range of acetate fabrics, including rigid knitted fabric and a wide range of woven cloths, has a winch roller at least partly submerged in the dye or other processing liquor. Means

are provided to create a flow of liquor in the beck to assist movement of the fabric, particularly movement away from the winch. This enables satisfactory movement of the fabric while imparting relatively low tension to it. It also enables a relatively deep beck to be used even when the material tends to float in a normal winch machine. C.O.C.

Continuous Treatment of Fibres with Organic Gaseous Materials
T. Takagi *BP* 863,219 (20 Dec 1957)

The entry and exit from the treatment chamber have a device to prevent escape of the organic gas, an inert gas which takes no part in the reaction, e.g. air, being forced into this device. C.O.C.

Stenter Clips
Spooner Dryer & Engineering Co. *BP* 863,825 (15 May 1958)

Describes stenter clips especially suitable for machines for heat-setting of nylon, Terylene, and other thermoplastic materials. The clips enable the machine to be used as either a clip or a pin stenter. C.O.C.

Drying Fibrous Webs
Gebrüder Sucker *BP* 865,115 (Germany 24 July 1956)

Describes an arrangement of drying ducts whereby the size of the dryer is reduced. C.O.C.

Drying Travelling Webs
Timsons and Coates Brothers & Co. *BP* 868,680 (9 Feb 1959)

Paper, cloth, films, etc. are dried after printing in a two-web apparatus. Side plates, set close to the longitudinal edges of the webs, retain the heat within the confined space between the webs. R.A.

Nozzles of Heat-treatment Apparatus for Cloth and other Webs
G. Mohring *BP* 864,149 (Germany 26 July 1958)

The width of the nozzle outlet is made adjustable at at least three points along the depth of the nozzle. This enables accurate control of the quantity of heat and air delivered by the nozzles. C.O.C.

Control of Drying Apparatus
Fleissner & Sohn Maschinenfabrik *BP* 866,596 (Germany 27 June 1956)

Describes control mechanism which enables the final moisture content of the material being dried to be accurately regulated independently of the temperature in the dryer and the speed of the material through it. C.O.C.

Drying Rollers for Paper Felts
S.R.R.I. Société de Recherches et de Réalisations Industrielles *BP* 868,865 (France 4 Oct 1957)

The central core carries radial channels and the housing has a distributor chamber for the drying fluid, so that instead of a circular flow of fluid around the bearing, a flow parallel to the axis is set up. R.A.

Compressive Shrinkage Machine
Bradford Dyers' Association *BP* 860,885 (16 May 1956)

In a machine where the fabric is pressed between a contractible belt and a heated roller or where it is nipped by two rollers and fed into a very narrow passage from which it is forced to emerge more slowly than it enters and in which it is prevented from buckling, passing the fabric partly around a heated nip roller before it enters the nip much increases the speed at which the machine can be run. It also enables the amount of shrinkage that can be produced to be increased. The fabric can enter the machine in a damper condition than where the fabric is not preheated, e.g. the moisture content of a cotton cloth may be 22% instead of the 14% customary where preheating is not carried out.

BP 863,979 (18 July 1956)

In a compressive shrinking machine using a contractible belt, the changing of belts is simplified by having supporting members in which the shafts of the belt rollers can slide clear of the side frames, one or both of these members at one side of the machine being detachable so that the belt can be removed axially after the belt rollers have been moved clear of the side frames.

BP 864,063 (15 Aug 1957)

Belt changing is much simplified by mounting the shaft of one of the belt rollers to slide in and finally clear of guides in the side frame and in so doing to reduce the distance between the axes of the belt rollers. Means are provided for then interconnecting the two rollers so that the sliding roller becomes suspended from the other roller and the two can be handled as a unit. The unit is then lifted bodily out of the side frames or swung clear of one of them, for which purpose the upper roller must be released from the side frames or one end released from one side frame so that it can swing about a vertical axis in the other side frame. C.O.C.

Embossing Calender
Dornbusch & Co. *BP* 863,872 (Germany 26 Apr 1957)

Any fabric is neatly and clearly embossed by using an embossing roll of the same size and pattern as an embossing roll having a metal jacket, but having a jacket of an elastically yieldable synthetic material, e.g. polyvinyl chloride. The pressure needed for the embossing is much lower than that needed when a metal-jacketed roll is used. C.O.C.

Resilient Calender Bowls
Dornbusch & Co. *BP* 862,800 (Germany 7 Dec 1956)

A bend-resistant core is covered with a jacket composed of several layers of resilient material, e.g. paper, fabric, fleece, etc. These layers are produced by spirally winding on to the core a strip of the resilient material, applying a binding agent to the strip, preferably before winding it, and then applying uniform all-round external pressure to the wound strip in a direction at right angles to its surface. Such a bowl is much more resistant to mechanical stress in use than those hitherto available. C.O.C.

Controlling the Temperature of a Heat-exchange Roll in a Calender
Farrell-Birmingham Co. *BP* 861,188 (U.S.A. 2 May 1958)

A roll which is heated electrically and is maintained at constant temperature by circulating cooling air through it under pressure and in contact with the heating elements. C.O.C.

Extrusion Coating Apparatus for Paper, Cloth, etc.
Lowe Paper Co. *USP* 2,944,586 (20 Apr 1956)

A film of molten plastic is extruded into a substrate, the film being wider than the substrate. Thin, narrow belts to which the plastic will not adhere are placed upon the opposite ends of the rubber-backing roll. By this means the beneficial live properties of the rubber backing are retained, the thickened edges of the film are not formed on the substrate and can be trimmed off and recovered for further use without loss of substrate, and the plastic does not come into contact with the rubber roll to which it would adhere. C.O.C.

Heat-stabilising and Setting Tubular Fabrics
Wolsey *BP* 862,301 (12 Apr 1957)

The fabric is continuously drawn between a stretcher and rollers supporting the stretcher. It is then drawn over the stretcher and then through draw-off rollers close to the output end of the stretcher. Radiant heat is applied around and near to the stretcher to heat the fabric to at least its stabilising temperature as it passes over the stretcher. The fabric is cooled before it is drawn off the stretcher. C.O.C.

Apparatus for Spraying Textile Articles on Forms
Maschinenfabrik Eugen Bellmann *BP* 863,188 (Germany 26 Mar 1958)

Apparatus for spraying textile articles on forms within a chamber. The spray head is formed from tubes having nozzles directed against the parts to be treated. The tubes are so arranged that they conform to the shape of the forms. C.O.C.

Apparatus Sensitive to the Water Content of Vapour above Drycleaning Solvents
Chemische Fabrik Stockhausen & Cie *BP* 867,811 (19 Aug 1958)

Transfer Positive Films for Textile Printing Rollers (IX p. 392)
Drying Paper Webs (XI p. 396)
Web Drying (XI p. 396)

II— WATER AND EFFLUENTS

Water Analysis (XIV p. 397)

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Complexing Agents. V— 2,2′-Diaminodiethylether-*N,N,N′,N′*-tetra-acetic Acid

V. G. Yashunskii, D. D. Smolin, V. G. Ermolaeva, and M. N. Shchukina

Zhur. obshch. khim., **30** (Dec 1960) 3916–3918

Condensation of 2,2′-dichlorodiethylether with potassium phthalimide in presence of a little diethylamine gave 2,2′-diphthalimidodiethylether (96%), which on decomp. with 100% hydrazine hydrate afforded 2,2′-diaminodiethylether, isolated as its hydrochloride (78%). The latter on condensation with chloroacetic acid provided 2,2′-diaminodiethylether-*N,N,N′,N′*-tetra-acetic acid. G.J.K.

Detergents and Lubricants for Wool

W. S. Buck *J. Textile Inst.*, **52** (Mar 1961) P119–P129

The development of surface-active agents and their application in wool scouring and lubrication in Germany is traced from 1917 to date with special reference to non-ionic agents. Brief reference is made to alkyl naphthalene sulphonates, alkyl sulphates, acyl isethionates, taurates, sarcosinates, alkyl and alkaryl sulphonates and alkaryl-polyglycol ethers and their salient properties are noted. Non-ionic agents are considered in terms of polyoxyethylated nonylphenol and the relation between degree of oxyethylation and wetting power, cotton and wool detergency, and emulsifying power is described. Optimum ethylene oxide content (moles per mole nonylphenol) is, for mineral oils 4–8, for aromatic hydrocarbons 8–13, for neutral fats 10–13, and for fatty acids and waxes 23–30. A large proportion of wool scoured in Germany is now scoured with non-ionic detergents and the opinion that scouring at the isoelectric point (pH 4·9) minimises damage is gaining favour, but alkaline scouring is still the usual practice. Oleic acid and glyceride oils were replaced as wool lubricants on the grounds of internal economy by mixtures of mineral oil and non-ionic agents. These now command the bulk of the German market for wool lubricants. They confer antistatic properties during spinning but are less effective than the water-soluble lubricants now being developed to obviate the defects arising from the use of mineral oils in the dyeing and finishing of blends of wool with synthetic-polymer fibres. The water-soluble lubricants are formulated to be stable during processing, including steaming, but yet readily removable in the final stages. The various polyethylene glycols (mol. wt. 200–2000) show inadequate lubricating properties, cause corrosion of machinery, and are subject to fungal attack even in presence of fungicides. Recent developments have been based on mixtures of an amino-carboxylic acid derivative of a fatty acid with a phosphate triester of a polyoxyethylene derivative. Lubricants of this type, now in use in Germany, e.g. Lanigen Lubricant SG, are water-soluble, non-substantive and relatively non-corrosive. They are normally used at 4–7% on the fibre and are not prone to spontaneous ignition. After spinning the lubricant is converted to an active detergent by addition of a little ammonia or soda to the aqueous bath. E.C.

Structure of Hydrocarbons and their Solubilisation in Solutions of Sodium Soaps of Saturated Fatty Acids

P. A. Demchenko and A. V. Dumanskii

Doklady Akad. Nauk S.S.S.R., **134**, No. 2 (11 Sept 1960) 374–375

The limiting solubility of the undermentioned aromatic and aliphatic hydrocarbons in 0·1-M soln. of sodium caprylate, caprate, laurate, myristate, palmitate, and stearate is found to decrease in the series: benzene > toluene > styrene > *o*-xylene > ethylbenzene > heptane > iso-octane > octane. It would appear that the tendency for the formation of oleophilic micellar structures, capable of bonding larger quantities of hydrocarbon per volume of aq. soln., increases with increasing chain length of the soap homologues. G.J.K.

PATENTS

Stabilisation of Per-compounds

Gy *BP* 866,492 (3 May 1957)

Chelating agents of formula

$$(HOOCCH_2)_2N{\cdot}CH_2{\cdot}CH_2\left[N(CH_2COOH)CH_2CH_2\right]_n N(CH_2COOH)_2$$

are good stabilising agents for per-compounds, e.g. Na perborate, and have the advantage of not being readily attacked by per-compounds in aqueous solution. C.O.C.

Bleaching Composition for Stain Removal

Unilever *BP* 864,798 (20 Mar 1958)

A free-flowing solid bleaching composition comprises an inorganic per-salt and a solid reactive aliphatic carboxylic ester. The ester particles are such that ⩽ 70% of the ester is retained on a 60 mesh BS sieve. C.O.C.

Polyquaternary Compounds for Improving the Wet Fastness of Direct Dyeings

FBy *BP* 869,423 (Germany 8 Sept 1956)

Compounds of formula

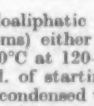
$$n{\cdot}R^1R^2N{\cdot}R^3{\cdot}X \rightarrow [-NXR^1R^2{\cdot}R^3-]_n$$

($n > 2$; R^1 and R^2 = same or different hydrocarbon radicals or together with the N atom form a ring; R^3 = hydrocarbon radical which may contain one or more hetero-atoms; X = Hal) are obtained by treating a compound of formula $R^1R^2N{\cdot}R^3{\cdot}X$ with water. They are used for improving the wet fastness of direct dyeings. C.O.C.

Water-soluble Basic Nitrogenous Resins for Increasing the Wet Fastness of Direct Dyes on Cellulose

Gy *BP* 865,686 (Switzerland 27 May 1957)

The products are obtained by heating compounds of formula



(A = aliphatic or cycloaliphatic containing $\alpha\beta$-C atoms attached to the N atoms) either alone or with organic solvents of b.p. 120–200°C at 120–280°C until about half a mol. of NH_3 per mol. of starting product is split off. If desired they may be condensed with formaldehyde or a triazine compound containing > 1 mol. Hal. They are used to increase the wet fastness of direct dyeings on cellulose without affecting the hue or fastness to light. C.O.C.

Modified Starch Sizes

National Starch & Chemical Corpn. *USP* 2,946,705 (26 Aug 1958)

Starch derivatives, e.g. esters or ethers, containing an amine group are much more efficient warp-sizing agents than starch itself, their solutions being more stable, and their lubricating effect much greater. They also have an antistatic action. C.O.C.

Graft Copolymers of Granular Starch

A. E. Staley Manufacturing Co. *BP* 869,501 (U.S.A. 13 Mar 1959)

A granular, unpasted amylaceous material is treated with an ethylenically unsaturated monomer, e.g. vinyl-acetate and ethyl acrylate, in presence of an oxidising polymerisation catalyst, e.g. $K_2S_2O_8$. This enables production of a wide range of products having most varied uses, e.g. as sizes for textiles and paper. C.O.C.

Water-soluble Interpolymers of Acrylic Acids and 2-Ethylhexyl Acrylates— Sizes for Nylon

Monsanto Chemical Co. *USP* 2,945,013 (22 Mar 1956)

Interpolymers consisting of 93·5–98·5 mol. % of acrylic acid and/or methacrylic acid and 6·5–1·5% of 2-ethylhexyl acrylate and/or 2-ethylhexyl methacrylate are used as sizes for nylon. C.O.C.

Copolymers

Ciba *BP* 864,311 (Switzerland 22 Mar 1957)

Copolymers of (*a*) an aliphatic acid containing at least one functionally converted COOH group in which the >C=O group of the acid is bound to a hetero atom which itself is bound through a bridge of > 1 C to a tertiary or quaternary N atom, and any other residues bound to such basic N atom contain no more –COO– groups than are present in the first-mentioned acid, and (*b*) a compound of formula $CH_2{:}CR^1{\cdot}CO{\cdot}NR^2R^3$ (R^1 = H or Alk of 1 or 2 C; R^2 = H or an organic radical; R^3 = an organic substituent; when R^2 = H then R^3 is bound to the amide N through a secondary or tertiary C atom) and, if desired, (*c*) an ethylenically unsaturated compound, have a wide range of uses as

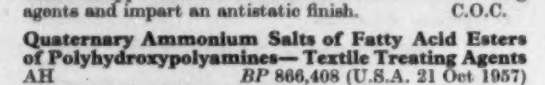
textile sizes and finishes, protective colloids, dispersing agents, etc. 20 Examples are given. C.O.C.

Phosphate Antistatic Agents having Softening and Emulsifying Properties
American Viscose Corpn. *USP* 2,945,774 (4 Apr 1956)

The products obtained by treating an aliphatic polyamine with oleic acid, then crosslinking the resulting oleylamidoalkylamine with carbamic acid, which may be 2-substituted, e.g. urea, and finally heating in presence of phosphoric acid or an alkyl phosphoric acid, are soluble in oil, for which they also act as emulsifying agents. Such solutions applied as textile lubricants also act as softening agents and impart an antistatic finish. C.O.C.

Quaternary Ammonium Salts of Fatty Acid Esters of Polyhydroxypolyamines—Textile Treating Agents
AH *BP* 866,408 (U.S.A. 21 Oct 1957)

Compounds of formula



(R = H or aliphatic acyl of 12–18 C but at least one must be the latter; M = monovalent hydrocarbon of 1–4 C attached to a tert. N atom in the polyamine chain so as to form a quaternary ammonium group; A = alkylene of 2–6 C; n = 2, 3 or 4; p = 0–4; y = 1 to p + 2; X = anion) have wide uses as textile assistants. Thus the quaternary ammonium salt obtained from *N*-(β-hydroxyethyl)-*NN'N'*-tris(β-hydroxypropyl)-ethylenediamine tristearate and dimethyl sulphate is a good softening and antistatic agent for nylon. 20 Other examples are given. C.O.C.

Antiseptics
Joh. A. Benckiser G.m.b.H. Chemische Fabrik *BP* 861,043 (Germany 26 Oct 1956)

Compounds of formula $R^1R^2N{\cdot}CS{\cdot}S{\cdot}R^3$ (R^1 and R^2 = aliphatic or aromatic group or together form part of a ring; R^3 = metal, amine, a salt- or carbamate-forming group, or $-S{\cdot}CS{\cdot}NR^4R^5$ (R^4 and R^5 are same or different, as R^1 and R^2)), e.g. tetramethylthiouram disulphide, have good bacterio- and fungi-static properties. Their action is markedly enhanced if they are used in conjunction with condensed phosphoric acids or their salts. They are particularly suitable for adding to paper pulp in the beater, and for use in cotton wool, bandages, etc. C.O.C.

Maleic Anhydride–Vinyl Alkyl Ether Copolymers
General Aniline *BP* 863,379 (U.S.A. 19 Feb 1957)

Copolymers of the above type in which ≮ 10% of the COOH groups have been converted to ester groups are compatible with polyvinyl methyl ether in all proportions. Such mixtures are of use *inter alia* as textile sizes which are readily removed by simple treatment with water, as impregnants and coatings for paper where temporary wet strength is desired, and as adhesives. C.O.C.

Aminoplast Textile Finishing Composition
British Industrial Plastics *BP* 865,319 (28 July 1958)

Modification of *BP* 607,950 (J.S.D.C., 65 (1949) 94). Replacement of the alkylated methylolmelamine by 1,3-bis(hydroxymethyl)iminazolid-2-one or its water-soluble wholly or partly alkylated derivatives, e.g. 1,3-bis(methoxymethyl)iminazolid-2-one, results in a finish which is less liable to retain chlorine and which does not yellow when treated with hypochlorite. C.O.C.

Cationic Aminoplast Resins—Tanning Agents, Textile Assistants, etc.
Nopco Chemical Co. *BP* 866,411 (U.S.A. 4 Nov 1957)

2·5–3·5 Moles HCHO, 1 mole dicyandiamide and water are mixed with enough of a water-soluble carboxylic acid to bring the mixture to pH < 2·5. The mixture is then heated to 96°C while keeping pH < 7·0. Urea is then added in amount at least equal to that theoretically required to form monomethylolurea with the unchanged HCHO, and the mixture is then refluxed for ≯ 5 h. The products have excellent tanning properties, yielding a white, plump leather of good fastness to light and having a relatively high shrinkage temperature. They are also useful on textiles as water-repellent and crease-recovery agents. C.O.C.

Combined Finishing and Water-repellent Agents
BASF *BP* 863,748 (Germany 3 Dec 1957)

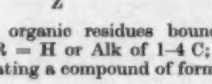
A combined stiff and water-repellent finish suitable, e.g., for awnings, tent and umbrella cloths, and washable tablecloths, is obtained by use of a mixture of (*a*) an aqueous solution of a copolymer of (i) 10–95% of methacrylamide, (ii) 5–45% of an ester of an ethylenically unsatd. carboxylic acid and/or an ethylenically unsatd. nitrogenous basic compound, and, if desired, (iii) ≯ 85% of one or more other amides of ethylenically unsatd. carboxylic acids, and (*b*) an aqueous dispersion of alumina gel or zirconium oxide gel. Such a mixture is stable even after prolonged standing. C.O.C.

Polymeric Phosphonitrilic Chlorides—Flame-resisting Agents
Fran *BP* 865,396 (France 1 Aug 1956)

The products obtained by treating 1 mol. of PCl_5 with ≮ 1 mol. of anhydrous NH_3 or NH_4Cl are water-soluble. Textiles, etc., impregnated with such a solution, dried, and heated in air at > 100°C are given a flame-resisting finish which has excellent fastness to water, weathering, and repeated washing. C.O.C.

Organic Phosphorus Compounds
Ciba *BP* 863,380 (Switzerland 15 Feb 1957)

Compounds of probable formula



(A^1 and A^2 = organic residues bound to P through C, O, S or N; R = H or Alk of 1–4 C; Z = O or S) are obtained by treating a compound of formula $A^1A^2P{\cdot}NHR$, ‖ Z

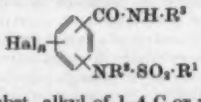
e.g. *OO'*-diethylamidophosphate, with chloral. They have varied uses as pesticides, flame-resisting agents, textile assistants, and plasticisers. C.O.C.

Pyridine-3-sulphonic Acid and Benzimidazole as Mothproofing Agents
Hightower Morse & Co. *USP* 2,945,735–6 (17 Dec 1957)

Presence of ≮ 0·5% of pyridine-3-sulphonic acid or benzimidazole in keratinous fibres imparts a mothproof finish which is fast to washing and dryecleaning. The agents are applied from acid, neutral, or alkaline aqueous solution, but are especially suitable for use in acid dyebaths. C.O.C.

***N*-Sulphonylated Aminobenzoic Acid Acylamides as Mothproofing Agents**
Gy *BP* 865,735 (Switzerland 24 Dec 1957)

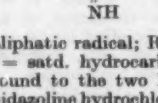
Compounds of formula



(R^1 = halogen-subst. alkyl of 1–4 C or phenyl or phenylalkyl nuclearly substituted by Hal and/or trifluoromethyl; R^2 = H or Alk of 1–4 C; R^3 = C_6H_5, phenoxyphenyl or phenylmercaptophenyl subst. by Hal and/or trifluoromethyl; n = 0–4; Hal = Cl or Br) e.g. 2-(3',4'-dichlorobenzenesulphonemethylamido)-5-dichlorobenzoic acid-3'',4''-dichloroanilide, are excellent mothproofing agents. They can be applied in the dyebath, sprayed on to the fibres, or applied from organic solvent solution. C.O.C.

Heterocyclic Nitrogenous Antiseptics
Gy *BP* 865,675 (Switzerland 28 Dec 1956)

Compounds of formula



(R^1 = lipophilic aliphatic radical; R^2 = H, Alk of 1–5 C or cyclohexyl; A = satd. hydrocarbon of which αβ- or αγ-C atoms are bound to the two N atoms) are e.g. 1-dodecyl-2-iminoimidazoline hydrochloride. They are soluble in water and some organic solvents. They can be used for disinfecting textiles and for rendering them sterile for prolonged periods. The treated textiles do not tend to yellow on prolonged storage or exposure to light. C.O.C.

Water-soluble Cationic Resins
Borden Co. *BP* 861,024 (26 Aug 1957)

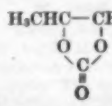
A mixture of (1) the partly condensed, water-soluble viscous cationic material obtained by heating an acidified aqueous solution of 0·33–1·0 mol. of an aliphatic polyhydric alcohol containing 2–6 OH groups and 1 mole of epichlorohydrin until reaction becomes slow, then adding 1 mole of an aliphatic polyamine containing 2–5 amino groups and continuing heating, and (2) 1·5–4·0 moles of HCHO and 1 mole of urea, the proportion of (1) being 1–3 times the weight of urea, is heated at $\leq$ 40°C at pH 1·5–10·0 until the mixture becomes viscous. Finally the mixture is brought to pH 7–8. The resulting cationic resin is very soluble in water and of good strength and durability, and highly stable chemically. It is particularly useful for imparting high wet strength to paper. C.O.C.

Compositions Containing Polyvinylpyrrolidone and Alkylated Phenols
General Aniline *BP* 862,239 (U.S.A. 8 Nov 1956)

A mixture of an alkylated phenol and a polyvinyl pyrrolidone or a copolymer of a vinyl pyrrolidone is soluble in water and in many organic solvents. It is film-forming and has a wide range of uses, e.g. as a plasticiser for many resins, as a protective coating for metals, a size for glass fibres, a dispersing agent for pigments in polyethylene, etc. C.O.C.

Solvent for Vinyl Chloride–Vinyl Acetate Copolymers
American-Marietta Co. *BP* 865,688 (24 June 1958)

A mixture of benzene and/or toluene and/or xylene containing 9–75% by wt. of propylene carbonate



is a good solvent for vinyl chloride–vinyl acetate copolymers. Solutions obtained by its use are good bases for coating compositions. C.O.C.

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Reactive Methylene Compounds
H. G. Garg

V—Condensation with Benzenediazonium Salts
J. Indian Chem. Soc., **38** (Feb 1961) 113–114

The following benzeneazo-deriv. (benzeneazo-, 4-methoxy-, 4-bromo-, 4-, 3- and 2-chloro-, 4- and 3-nitro-, 4- and 3-methyl-, 2-chloro-4-nitro- and 2-nitro-4-chloro-) of 4-chloro-, 4-bromo-, 4-methyl-, and 4-methoxybenzoylacetone are described. The rate of coupling increases when chloro and bromo groups are present in *p*-position in the phenyl group, whereas methyl and methoxy groups decrease the rate. All the cpd. are highly coloured cryst. solids which give a red colour with conc. H_2SO_4.

VI—Title as V
Ibid., 115–116

The 12 benzeneazo-deriv. (above) of 4-chloro-, 4-bromo-, 4-methyl-, and 4-nitro-dibenzoylmethane are described. They are highly coloured cryst. solids which develop a red colour with conc. H_2SO_4. H.H.H.

Intramolecular Hydrogen Bonding and Dipole Moments of Organic Compounds

VII—Phenylazo-, Carboxyl-, and Methoxycarbonyl-substituted Naphthols
A. E. Lutskiĭ, L. A. Kochergina, and B. A. Zadorozhnyĭ
Zhur. obshch. khim., **30** (Dec 1960) 4080–4084

Dipole moments of the following in benzene and dioxan have been determined at 25°C—1,2-, and 1,4-phenylazonaphthols and their methyl ethers; 1,2- 2,3- and 1,4-hydroxynaphthoic acids and their esters and ethers. The results indicate the presence of strong intramolecular hydrogen bonding in 1,2-phenylazo- and 2,3-carboxy- or methoxy-carbonyl-substituted naphthols, but weaker bonding in 2-carboxy-3-methoxynaphthalene. The positive value of $\Delta\mu$ ($= \mu_{C_{10}H_6XY} - \mu_{C_5H_4XY}$), where the two substituents are in the same ring, is attributed to an increase (*a*) in double-bond character of C_1–C_2 and C_3–C_4 in naphthalene and (*b*) induced moments in functional groups; and also to the steric effect of *peri* hydrogen atoms.

VIII—2,4- and 4,6-Diacetylresorcinols and their Methyl Ethers
A. E. Lutskiĭ, L. M. Volova, and P. A. Chernyavskiĭ
Ibid., 4085–4088

The results of dipole measurements on 2,4- and 4,6-diacetylresorcinols and their dimethyl ethers in benzene and dioxan at 25°C are consistent with the presence of two intramolecular hydrogen bonds. G.J.K.

Spectrophotometric Study of Chelate Formation by Interaction of Sexivalent Chromium and Alizarin Red S
S. K. Banerji and A. K. Dey
J. Indian Chem. Soc., **38** (Feb 1961) 121–126

The pink chelate formed by interaction of Cr (VI) with sodium alizarin-3-sulphonate (Alizarin Red S (C.I. 58005)) has composition 1:1 when determined by the method of continued variation using spectrophotometric measurements; it has max. absorption at 515 mμ and is stable between pH 3·5 and 8·0. The stability as determined by the authors' method (cf. *ibid.*, **34** (1957) 461) is $\Delta F^\circ = -6{\cdot}52 \pm 0{\cdot}35$ kcal. at 25°C. H.H.H.

Replacement of Sulphonate Groups by Hydroxyl in the Aromatic Series. VI—Decomposition of the β-Naphthol formed in the Alkali Fusion of Naphthalene-β-sulphonic Acid
N. N. Vorozhtsov and S. M. Shein
Ukrain. khim. zhur., **26** (No. 4) (1960) 490–495

Decomp. of the β-naphthol formed in the alkali fusion of sodium-β-naphthalene sulphonate yields at 360–400°C naphthalene, liquid hydrocarbons, *o*-toluic acid, β-*o*-tolylpropionic acid (I) and other products. The change in the composition of the reaction products with time indicates that carboxylic acids are primary products, whilst the liquid hydrocarbons and naphthalene are final products of the decomp. I has been obtained by reduction of β-*o*-tolylacrylic acid with hydrazine hydrate in ethanol in the presence of Raney Ni. The amide and hydrazide of I are described. G.J.K.

Isomerisation of Azoxy Compounds using Labelled Oxygen
M. M. Shemyakin, Ts. E. Agadzhanyan, V. I. Maĭmind, R. V. Kudryavtsev, and D. N. Kursanov
Doklady Akad. Nauk S.S.S.R., **135** (11 Nov 1960) 346–349

The results obtained on isomerisation of azoxybenzenes (I) using ^{18}O oxygen (either in I or in the acid reaction medium) taken in conjunction with those obtained previously with ^{15}N-labelled cpd. (M. M. Shemyakin et al., *Izvest. Akad. Nauk S.S.S.R., otdel. khim. nauk*, (1960) 866) enable the following conclusions to be drawn: *p*-hydroxyazo cpd. result from intermolecular rearrangement, whilst intramolecular processes are responsible for the formation of *o*-hydroxyazo cpd. and also for the transformation of β forms of azoxy compd. into α forms. The latter reaction and also the formation of *p*-hydroxyazo cpd. can be readily understood on the basis of the intermediate formation of C_6H_5—N—N—C_6H_5 (O). G.J.K.

Phototropy in Dyes: Relation Between Degree of Aggregation and Phototropy
G. Eigenmann and F. Kern
Textil-Rund., **16** (Apr 1961) 167–176

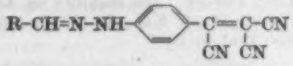
A typical absorption spectrum of a phototropic dye is given and the method of measuring phototropy explained. Next the absorption curves of some phthalocyanine sulphonic acids, dissolved in water, sodium chloride solution, polyethylene oxide solution, or alcohol are given and two peaks on the curve are shown to correspond to the monomolecular and aggregated dye, respectively. From these a measure of the degree of dispersion is obtained. In a similar way the degree of aggregation is shown to be approximately the same in dyed cellulose sheet. Synthetic resins applied to the sheet are shown to act as dispersing agents. The smaller the degree of aggregation, the greater is the tendency to phototropy. P.B.S.

Cyanocarbon Chemistry. XVIII— Tricyanovinylation of Hydrazones and other Nucleophilic Substances

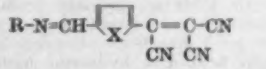
J. R. Roland and B. C. McKusick

J. Amer. Chem. Soc., **83** (5 Apr 1961) 1652–1657

The strong electrophilic nature of tetracyanoethylene is shown by reaction with a wide range of nucleophilic substances, e.g. aromatic hydrazones, azulene, pyrrocoline and 2-methylfuran. The tricyanovinyl products are dyes, ranging in colour from blue to yellow, which possess greatest affinity for cellulose acetate, silk and nylon. Polyethylene terephthalate and polyacrylonitrile can be dyed to medium and full depths. Unlike the *p*-tricyanovinylarylamines (C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **82** (1960) 6132), the tricyanovinylphenylhydrazones are resistant to alkali. They may be prepared by two general methods— (*a*) stirring a phenylhydrazone with tetracyanoethylene in a strongly polar solvent (e.g. dimethylformamide) at 20–60°C, or (*b*) refluxing a carbonyl cpd. with 1-formyl-2-*p*-tricyanovinylphenylhydrazine in aq. alcoholic soln. containing hydrogen chloride. The majority of products have the general formula



where R is propyl or phenyl. The phenyl group may also be substituted by *p*-CH_3, *p*-Cl, *o*-OH, 2,4-$(OH)_2$, 3,4-$(CH_3O)_2$, *p*-$(CH_3)_2N$, *p*-$(C_2H_5)_2N$, $C_6H_5CH{=}CH$, 2-furyl, 5-methyl-2-furyl, 2-thenyl, 2-pyrryl, 3-pyridyl, 3-indolyl or 3-isoxazolyl. Molar extinction coefficients (ϵ) of these cpd. exceed 20,000. Tricyanovinyl deriv. of furfural and pyrrole-2-aldehyde were prepared by method (*a*). General formula is



where X is O or NH and R is $-NHC_6H_5$, $-N(CH_3)_2$ or $-NHCONH_2$. λ_{max} for these cpd. lies between 500 and 580 mμ and ϵ exceeds 30,000 except where X is NH and R is $-NHC_6H_5$. Azulene reacts easily by method (*a*) to give 1-tricyanovinylazulene with λ_{max} at 490 mμ and ϵ = 26,800. Pyrrocoline gives a product of similar colour, and 2-methylfuran condenses with tetracyanoethylene in 5-position in good yield (λ_{max} = 440 mμ, ϵ = 26,900). In contrast furan itself is not tricyanovinylated under these conditions. F.J.

How to make Azo Pigments

N. P. Chopey *Chem. Eng.*, **68** (1) (1961) 74–77

Chem. Abs., **55** (20 Mar 1961) 5807

Plant for production of azo pigments is described and a flow sheet given for production of Lithol Rubine (C.I. 15850 Ca lake). C.O.C.

Insoluble Azo Dyes

L. N. Nikolenko and K. K. Babievskii

Zhur. priklad. khim., **33** (Oct 1960) 2373–2374

Coupling of the diazonium chloride of alkyl-(4-aminophenyl)-ketones (I) or 4-alkylaniline (II) with 2-naphthol gave red azo dyes of formula

(R = CH_3CO; $C_5H_{11}CO$; $C_7H_{15}CO$; $C_{11}H_{23}CO$; C_6H_{13}; C_9H_{17}; $C_{13}H_{25}$; or $C_{18}H_{37}$). Coupling of I or II with 1-phenyl-3-methyl-5-pyrazolone gave the corresponding orange and yellow dyes. G.J.K.

Spectroscopic and Quantum Theoretical Study of the Azo Dyes

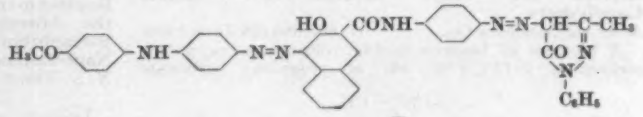
M. B. Robin *Univ. Microfilms* (Ann Arbor, Mich.) *L.C. Card* No. Mic 60-4299, 177 pp. *Dissertation Abstr.*, **21** (1960) 1393 *Chem. Abs.*, **55** (17 Apr 1961) 7035

Separation Components in the Synthesis of Azo Dyes XV— Preparative, Colour, and Spectroscopic Aspects in the Azotol Series

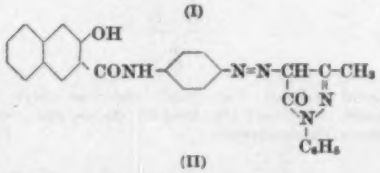
J. Reichel and W. Schmidt

Studii şi Cercetări Ştiinţe Chimice (Timişoara) **VII** (July–Dec 1960) 245–254

In continuation of previous work (cf. J.S.D.C., **76** (Nov 1960) 636) the separation effect of a central carbamido group is examined in the unsym. azo dye (I) when compared with the yellow (II, III, IV) and blue (V) dyes. Dyeings were developed on cotton with diazonium cpd. The absorption spectra in dioxan were recorded, and confirm the separation effect of the carbamido group, although the alteration in the max. of the bands and the increased intensity of the absorption indicate the effect to be incomplete.



(I)



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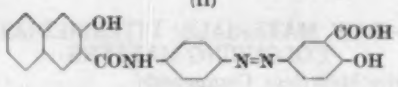

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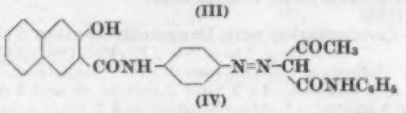

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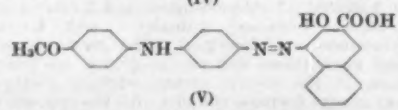
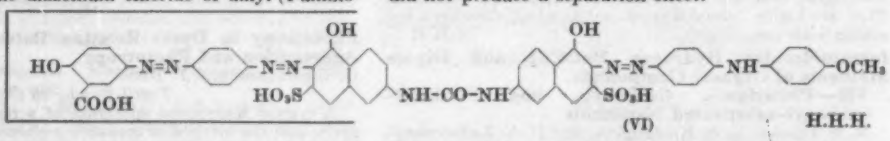


(V)

XVI— Effect of the Central Urea Group

J. Reichel and A. Demian *Ibid.*, 269–275

Dye VI was prepared and compared spectroscopically with relevant dyes, as in previous papers (cf. J.S.D.C., **76** (Nov 1960) 636). The data indicated that the urea group did not produce a separation effect.



(VI)

H.H.H.

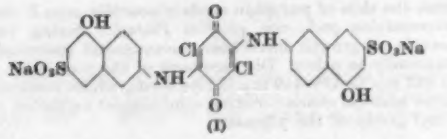
Dye Syntheses in the 1,4-Benzoquinone Series

J. Reichel and A. Balint

I— Arylamination of Chloranil with 2,5-Aminonaphthol-7-sulphonic acid

Studii şi Cercetări Ştiinţe Chimice (Timişoara) **VII** (July–Dec 1960) 255–261

The title reaction carried out in aq.-alcoholic soln. gave a good yield of the dye (I) which, when coupled with diazonium salts, afforded disazo dyes in yields of 76–93%. The disazo dyes had good affinity for wool and cotton in beautiful hues; 15 examples of developed dyes are given.

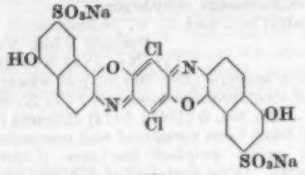


(I)

II— Ring Closure of Dye (I) above to form the corresponding Dioxazin Dye

Ibid., 263–268

Formation of dye (II) by oxidative ring closure of dye (I) is described, and its constitution established by synthesis; it gives reds to violet blues on cotton which can be developed by coupling with diazonium salts.



(II)

H.H.H.

Aromatic Diazo and Azo Compounds

XXXIX— Chromatographic Constitution Analysis of Synthetic Dyes

J. Panchartek, Z. J. Allan, and F. Mužík

Collection Czechoslov. Chem. Communs., **25** (1960) 2783–2799 (*in German*)

Chem. Abs., **55** (20 Mar 1961) 5499

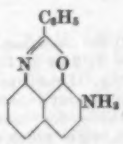
Reductive cleavage with HCl and chromatographic examination of the products were developed for the study of the structure of azo dyes. The behaviour of the cleavage products when heated with HCl at 150–250°C was also examined.

XL— Closure of the Oxazine Ring in Amino-peri-benzamidonaphtholsulphonic Acids. Synthesis of some peri-Naphthoxazine Derivatives

F. Mužík *Ibid.*, 2831–2840

Chem. Abs., loc. cit., 5500

Monoazo dyes obtained by coupling diazo compounds with 8-benzamido-1-naphtholsulphonic acids yield the 2-amino compounds when reduced with alkaline $Na_2S_2O_4$, but with $SnCl_2$ and HCl, oxazines



having 1 or 2 SO_3H groups in positions 3, 5 or 6 were obtained. Deamination and replacement of NH_2 by OH are described. E.S.

Sinagen Dyes and 50% Sinagen Dye Solutions

W. Siegrist *Textil-Rund.*, **16** (Apr 1961) 184–190

An explanation of the chemistry and development of Sinagen dyes (azoic dyes developed by neutral steam).

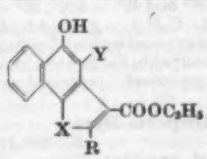
P.B.S.

Bromination and Azo Coupling of Naphthofuran and Benzindole Derivatives

A. N. Grinev, Khun' Shchi-tsyun', and A. P. Terent'ev

Zhur. obshch. khim., **30** (Dec 1960) 4030–4034

Bromination of 5-hydroxynaphthofuran deriv. with dioxandibromide and *N*-bromosuccinimide yields I



(I)

(R = CH_3 or C_6H_5; X = O; Y = Br). Bromination of 5-hydroxybenzindole deriv. under analogous conditions is more complex, yielding bromine-free cpd. and tarry polymers. Azo coupling of the deriv. of 5-hydroxy-naphthofuran and 5-hydroxybenzindole with diazonium salts gave in good yield a series of red dyes of formula I, where X = O, NCH_3, or NC_6H_5; Y = N=N·C_6H_4·NO_2(*m*) (or CH_3). Preparative details are given. G.J.K.

Steric Effects in Di- and Tri-arylmethanes. V— Electronic Absorption Spectra of Derivatives of Malachite Green containing *ortho*-Substituents in the Dimethylaminophenyl Groups

C. C. Barker and G. Hallas *J.C.S.*, (Apr 1961) 1529–1531

Spectral changes caused by the crowding effect of substituents in the 2′- and 2′,2″-positions of Malachite Green (C.I. 42000) are described and discussed. The increase in intensity of the *z*-band, which was found to occur [cf. *ibid.* (1961) 1285; J.S.D.C., **77** (July 1961) 323] when substituents were introduced into the 2-position, is now also found to take place when substituents are already in the 2′- and 2′,2″-positions. Bathochromic shifts of the *y*-band are attributed to the greater electronic symmetry along the *y*-axis which results from displacement of charge on to the phenyl group by rotation of the dimethyl-aminophenyl groups about the central bonds, and are analogous to those produced by methyl groups in the 3′,3″- and 3′,5′,3″,5″-positions [cf. *ibid.* (1960) 3790; J.S.D.C., **77** (Jan 1961) 30]. H.H.H.

Novel Cyanines. II— Trimethinecyanines and a Synthesis of 3-Aminopyridines

K. Dickoré and F. Kröhnke

Chem. Ber., **93** (1960) 2479–2485

Chem. Abs., **55** (6 Mar 1961) 4493

The vinylpyridinium salts from acylalkylpyridinium salts and CH_3·C_6H_5·N·CH:CH·CHO were converted into red trimethylcyanines of the anionocyanine type and into 3-pyridiniopyridine salts and thence to 3-aminopyridines. A.T.P.

Polymethine Dyes. VII— Polymethine Dyes Produced by Reaction of *p*-Dimethylaminocinnamaldehyde with Primary Aromatic Amines, Various Heterocycles, and Sulphonamides (Test for Sulphonamides)

M. Strell and S. Reindl

Arch. Pharm., **293** (1960) 984–991

Chem. Abs., **55** (3 Apr 1961) 6869

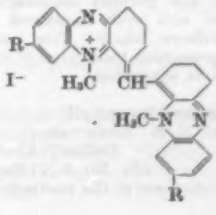
p-$(CH_3)_2NC_6H_4CH$:CHCHO (I) (525 mg) and *o*-$CH_3C_6H_4NH_2$ (321) in alcohol were treated with 60% $HClO_4$ (0·5), refluxed 10 min and stood overnight to yield a reddish violet polymethin. Similarly I and the following gave the corresponding polymethin dye (cpd. and colour): α-naphthylamine, green; 2-naphthylamine, silver grey; *p*-$NH_2C_6H_4COCH_3$, grey; anthranilic acid, blue; *p*-aminosalicylic acid, black; 2,4-dimethyl-5-carbethoxy-3-aminopyrrole, violet; barbituric acid (in methanol), blue; thiobarbituric acid (in methanol), violet; *N*-ethylrhodanine, violet; 1-phenyl-3-methyl-5-pyrazolone, reddish violet; *p*-$NH_2C_6H_4NHC$:N·CH:CH·S, reddish brown; *p*-$NH_2C_6H_4SO_2NHC$:N·N:C(C_2H_5)S, reddish brown; *p*-$NH_2C_6H_4SO_2NHC$:CH·CH:N·NC_6H_5, blue. C.O.C.

Cyanine Dyes from Phenazine Derivatives. III— Dyes from Tetrahydrophenazine

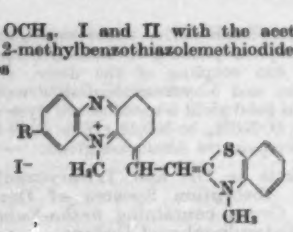
A. I. Kiprianov and E. A. Ponomareva

Ukrain. khim. zhur., **26**, No. 5 (1960) 633–636

Condensation of the quaternary salts of 1,2,3,4-tetrahydrophenazine (I) and of 1,2,3,4-tetrahydro-6-methoxyphenazine (II) with *p*-dimethylaminobenzaldehyde gave styryl dyes. I and II with sodium formate gave *s*-cyanine dyes



R = H, or OCH_3. I and II with the acetanilidovinyl deriv. of 2-methylbenzothiazolemethiodide gave *as*-cyanine dyes



The absorption max. of these dyes have been determined and a bathochromic shift has been found to occur for R = OCH_3. Preparative data are given. G.J.K.

Carbocyanine Dyes containing Benzimidazole Rings
J. Černík *Chem. listy*, **55** (1961) 44–62
Chem. Abs., **55** (3 Apr 1961) 6217

Discusses the suitability of benzimidazole cyanine dyes for colour photography, relations determining optical and photographic properties, effect of substituents on the absorption and sensitisation maxima of imidazole dyes, and preparation of carbocyanine imidazole dyes. 69 References. C.O.C.

Effect of the Solvent on the Colour of Dyes (Solvatochromism)
A. I. Kiprianov *Uspekhi Khim.*, **29** (1960) 1336–1352
Chem. Abs., **55** (17 Apr 1961) 7845

Review, 52 references, of the literature published in 1959, dealing mainly with colour changes in cyanine dyes in various solvents. C.O.C.

Indigoid Dyes. VII—Optical Determination of the Reversible Formation of the *cis*-forms of Symmetrical and Unsymmetrical Indigoids
R. Pummerer and G. Marondel
Chem. Ber., **93** (1960) 2834–2839
Chem. Abs., **55** (20 Mar 1961) 5957

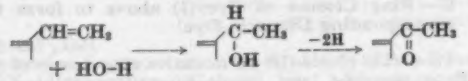
Change of absorption spectrum characteristic of *cis*-rearrangement was seen with selenoindigo by irradiation with orange light; the colour of the solution changed from bluish to yellowish red. The reverse rearrangement proceeds much slower than with *cis*-thioindigo, but can be effected within a few minutes by irradiation with a 25-w bulb. Change of oxindigo by irradiation with yellow light is also typical for a *cis*-rearrangement, but as it is not reversible this change is questionable. Unsymmetrical indigoids, e.g. Indigo Red or Thio Indigo Scarlet R (C.I. 73635), could not be rearranged similarly, but Ciba Scarlet G (C.I. 73860), which contains no NH groups, did undergo rearrangement. Ultraviolet spectra are given of Indigo (C.I. 73000), *NN'*-dimethylindigo, Thioindigo (C.I. 73300), selenoindigo, oxindigo and Thio Indigo Scarlet R. C.O.C.

Production of Stable Caramels (C.I. Natural Brown 10)
A. L. Sokolovskiĭ, V. N. Nikiforova, R. Ya. Greĭser, A. I. Izrin, M. I. Afonin, and S. M. Zalivanskaya
Opyt, Ruboty Prom. Sovet. Narod. Khoz. Moskov. Gorodsk Ekon. Admin. Raĭona, (6) (1958) 28–32
Referat. Zhur., Khim., (1959) Abstr. No. 72989
Chem. Abs., **55** (20 Mar 1961) 5803

The carbohydrate composition of the syrup has much more effect on the nature of the caramel composition than has acidity, ash or pH of the syrup. With decrease of glucose in the syrup, the caramels tend to have decreased hygroscopicity. Use of syrup with lower content of reducing substances permits preparation of a caramel composition of residual moisture content > 3% (upper limit according to GOST specifications) without deterioration in quality, and also permits manufacture of caramels of lighter colour and with improved stability during storage, and reduces waste. The possibility of discontinuing the protective treatment of the surface of the exposed caramel is suggested. C.O.C.

Pigments of Protochlorophyll
T. N. Godnev and N. K. Akulovich
Doklady Akad. Nauk S.S.S.R., **134**, No. 3 (21 Sept 1960) 710–712

Acetone–ether extracts of the protochlorophyll pigment from the skin of pumpkin seeds (*Cucurbita pepo L. convar. giromontiina greb. var. oleifera Pietsch.*) during various periods of growth have been investigated spectrophotometrically in ether. Displacement of the main blue max. at 432 mμ to 438–440 mμ in ripe seeds, whilst maintaining other spectral characteristics, may suggest oxidation of the vinyl group of the pigment



G.J.K.

Pigments of the Green Sulphur Bacteria *Chloropseudomonas ethylicum*
E. N. Kondrat'eva and L. V. Moshentseva
Doklady Akad. Nauk S.S.S.R., **135**, No. 2 (11 Nov 1960) 460–462

Absorption spectra (350–800 mμ) of whole cells and of pigments of two recently discovered (V. N. Shaposhnikov *et al.*, *ibid.*, **129**, No. 6 (1959) 1424) cultures *Ch. ethylicum* 2K and 3C have been measured and compared with those of typical green sulphur bacteria (*Chlorobium thiosulfatophilum*). It is found that *Ch. ethylicum* contains pigments which are typical for green sulphur bacteria and that they contain a special type of chlorophyll.

G.J.K.

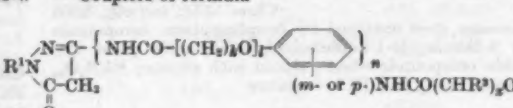
PATENTS

m-Dialkylaminophenols as Oxidation Bases for Dyeing Human Hair
Wella *BP* 868,325 (Germany 13 Nov 1958)

m-Dialkylaminophenols, particularly *m*-dimethylaminophenol, are excellent for obtaining drab to green oxidation dyeings in combination with 1,4-diaminobenzene or a nuclear substitution derivative thereof. The dyeings are fast to washing, light, weathering, and permanent waving. C.O.C.

Colour Couplers
Kodak *BP* 865,720 (U.S.A. 18 Sept 1956)

Couplers of formula

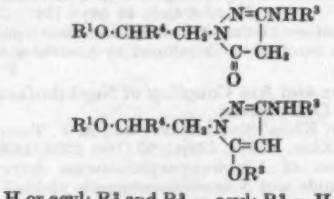


(m- or p-)$NHCO(CHR^3)_xOR^2$

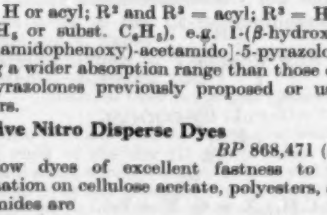
(R^1 = Alk of 1–12 C; R^2 = subst. or unsubst. benzene; R^3 = H or C_2H_5; k = 1, 2 or 3; l = 0 or 1; n = 0 or 1; x = 1, 2 or 3), e.g. 1-methyl-3-(4-[α-(2,4-di-t-amylphenoxy)butyramido]phenoxy)-acetamido-5-pyrazolone, are particularly suitable for use with benzoylacet-*o*-alkoxyanilide couplers, with which they yield yellow dyes having a wider absorption range than those obtained with previously known 1-alkyl-3-acylamido-5-pyrazolones.

BP 865,721 (U.S.A. 30 Oct 1956)

Colour couplers of formula



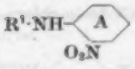
or



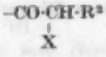
(R^1 = H or acyl; R^2 and R^3 = acyl; R^3 = H, Alk of 1–4 C or C_6H_5 or subst. C_6H_5), e.g. 1-(β-hydroxyethyl)-3-[(*p*-palmitamidophenoxy)-acetamido]-5-pyrazolone, yield dyes having a wider absorption range than those obtained from the pyrazolones previously proposed or used as colour couplers. C.O.C.

Reactive Nitro Disperse Dyes
ICI *BP* 868,471 (11 July 1958)

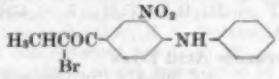
Yellow dyes of excellent fastness to washing and sublimation on cellulose acetate, polyesters, and especially polyamides are



(R^1 = carbocyclic radical which may be joined through a CO group in A to form an acridone ring; A may be substituted and A and/or B may contain a halogenoacyl group



(X = Cl or Br, R^2 = H or Alk)). They are obtained by condensing *o*-nitrohalogenobenzenes with carbocyclic primary amines (at least one reactant containing an acyl group $-CO\cdot CH_2R^2$), or, for the acridones, by condensing anthranilic acid with 2-nitro-1-halogenobenzenes containing a $-COCH_2R^2$ group, and dehydrating. The above are finally halogenated at low temperature in an inert organic solvent, optionally in presence of a catalyst. Thus, 2-nitro-4-propionyldiphenylamine (from aniline and 4-chloro-3-nitropropiophenone) is treated in $CHCl_3/AlCl_3$ with Br_2 at 20°C to give

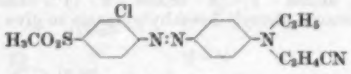


a reddish yellow dye of excellent fastness on acetate and nylon. A.T.P.

Orange Monoazo Disperse Dye

Ciba *BP* 868,143 (Switzerland 16 May 1957)

2-Chloro-4-methylsulphonyl aniline is diazotised and coupled to *N*-ethyl-*N*-cyanoethylaniline to give

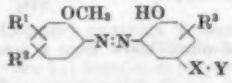


a bright yellowish red disperse dye of excellent fastness to light and sublimation. A.T.P.

Metal-complex Monoazo Dyes for Wool, etc.

BASF *BP* 865,410 (Germany 8 Nov 1956)

The 1:2 metal (especially Co or Cr) complexes derived from monoazo compounds

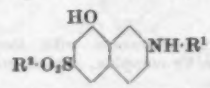


(R^1 = NO_2, COOH, SO_2H, SO_2Alk, SO_2Ar, OCH_3, sulphamyl or carbamyl which may be *N*-substituted; R^2 = H, Hal, CH_3, or OCH_3; R^3 = H, Hal, or Alk; X = CO or SO_2; Y = Alk, phenyl, OAlk, NH_2 or subst. NH_2 which may include a heterocyclic ring) either alone or combined with other coloured or colourless chelatable compounds, dye wool and nylon from weakly acid baths, or may be used for colouring cellulose ester lacquers, fibre-spinning solutions, etc. Thus the monoazo compound 2-amino-anisole-4-sulphonmethylamide → *p*-hydroxybenzanilide stirred in $\beta\beta'$-dihydroxyethyl ether with $Na_2Cr_2O_7$ gives the Cr-complex, which dyes wool bluish red. E.S.

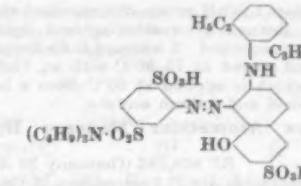
Red Monoazo Acid Dyes

S *BP* 864,742 (Switzerland 29 Aug 1958)

Orthanilic acid derivatives substituted in the 4-position by a sulphamyl group or by $SO_2\cdot Ar$ or $SO_2\cdot OAr$ are diazotised and coupled with derivatives of γ acid



(R^1 = H, or phenyl having *ortho* to the NH group 2 Alk radicals each of < 5 C and optionally other non-ionic substituents; R^2 = OH when R^1 = phenyl, or, when R^1 = H, R^2 = NR^3R^4; R^3 = H, cyclohexyl or Alk; R^4 = Alk, aralkyl, cycloalkyl or Ar, or R^4 with R^3 and N forms a saturated heterocyclic radical) to give red acid dyes applicable from neutral or weakly acid baths and of good wet fastness. Thus diazotised orthanilic acid-4-sulphondi-n-butylamide is acid-coupled with *N*-2,6-diethylphenyl-γ acid to give



which dyes wool, silk, and nylon claret. E.S.

Azo Acid Dyes having Halogenoacylamino Groups

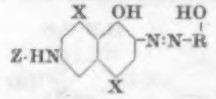
ICI *BP* 868,594 (23 June 1958)

The title dyes are mono- and dis-azo compounds free from SO_3H and COOH groups, and containing 1 or 2 groups $-NR\cdot CO\cdot X$ (R = H or Alk; X = halogenoalkyl, preferably CH_2Cl) and 1 or 2 sulphamyl, subst. sulphamyl, or alkylsulphonyl groups. Thus the monoazo compound sulphanilamide → 1-chloracetylamino-7-naphthol dyes wool orange from a neutral or slightly acid bath. E.S.

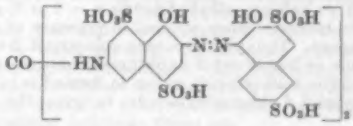
Copperable Azo Direct Dyes

FBy *BP* 866,914 (Germany 16 Aug 1956)

The title compounds have formula



(one X = SO_3H, the other = H or SO_3H; R = residue of *o*-coupling hydroxy compound, which may contain an azo group; Z = residue of monofunctional acylating agent of the aryl series, or residue of polyfunctional acylating agent (e.g. phosgene) linked with a second amino compound) and may be coppered in substance or on the fibre. Thus the monoazo compound 6-nitro-2-naphthylamine-4,8-disulphonic acid → R salt is coppered in presence of H_2O_2, and the nitro group is then reduced by means of Na_2S, which partially decoppers the dye. Condensation with phosgene, followed by treatment with a Cu salt, gives the copper complex of

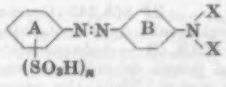


which dyes cotton reddish blue. E.S.

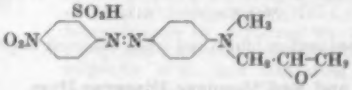
Monoazo Reactive Dyes for Cellulose

Ciba *BP* 868,026 (Switzerland 25 Sept 1957)

The title compounds have formula



(one or both X's = β,γ-epoxypropyl or β,γ-propylene chlorohydrin; the other X may be H or Alk; n = 1–3; A may contain Hal, Alk, NO_2, etc.; B may contain Alk, OAlk, etc.), and are similar to those claimed in *BP* 478,514 (J.S.D.C., **54** (1938) 284). They are applied in presence of an acid-binding agent. Thus the monoazo compound



applied to cotton in presence of NaCl and Na_3PO_4 gives red-violet. E.S.

Black Metal(Cobalt)-complex Monoazo Dyes for Anodised Aluminium

Ciba *BP* 868,595 (Switzerland 21 June 1957)

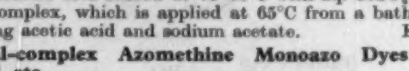
The 1:2 cobalt complexes of monoazo compounds nitro-*o*-aminophenol → *o*-coupling naphthylamine, and

containing at least 1 SO_3H group, dye anodised aluminium black of good fastness to weathering and light. Thus the monoazo compound 2-amino-4,6-dinitrophenol → naphthionic acid stirred at 75–80°C with aq. $CoSO_4$ gives the complex, which is applied at 65°C from a bath containing acetic acid and sodium acetate. E.S.

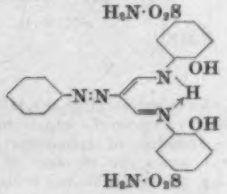
Metal-complex Azomethine Monoazo Dyes for Wool, etc.

BASF *BP* 868,284 (Germany 30 Apr 1957)

The title compounds are 1:1 complexes of Cu, Ni, Co, Fe, Zn, or Cr with dianils of tautomeric formulae



(R^1, R^2 = same or different phenyl or naphthyl radicals having OH or SH in *o*-position to the *N* atom, and possibly other substituents. They are prepared by condensing an *o*-hydroxy(or mercapto)phenylamine (or naphthylamine) with an arylazomalonodialdehyde, obtained e.g. by coupling a diazo compound with a β-aminoacrolein twice substituted on the *N* atom. Thus phenylazomalonodialdehyde and 2-aminophenol-4-sulphonamide are heated to 70–80°C in dimethylformamide. Addition of aq. nickel acetate gives the metal complex of

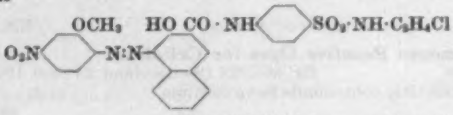


which dyes wool and nylon orange-yellow from an acid bath. E.S.

Monoazo Dyes having Halogenoalkyl Groups—Reactive Dyes for Cellulose

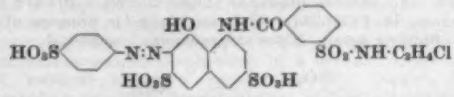
BASF *BP* 868,742 (Germany 17 Jan 1958)

Monoazo compounds $X(CO{\cdot}NH{\cdot}A{\cdot}SO_2{\cdot}NH{\cdot}Y)_n$ (X = residue of monoazo compound; A = subst. or unsubst. arylene; Y = halogenoalkyl of 2–4 C; *n* = 1 or 2) give fast dyeings on cellulose when applied in presence of an acid-binding agent. Thus the monoazo compound 2-amino-5-nitroanisole → 3-hydroxy-2-naphthoic acid is treated with $SOCl_2$ and the acid chloride group so formed is condensed with sulphanil-β-chloroethylamide to give the reddish blue



BP 868,745 (Germany 8 Nov 1957)

Water-soluble monoazo dyes containing 1 or 2 groups $-NH{\cdot}CO{\cdot}Ar{\cdot}SO_2{\cdot}NHR$ (R = halogenoalkyl of < 5 C give fast dyeings and prints on cellulose when applied with an acid-binding agent. Thus the monoazo compound sulphanilic acid → H acid (alkali-coupled) is condensed in presence of aq. Na_2CO_3 at 0–2°C with benzoyl chloride-*m*-sulphon-β-chloroethylamide to give

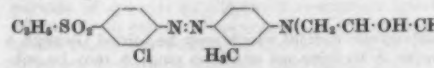


which dyes cotton bluish red when steamed in presence of Na_2CO_3. E.S.

Orange and Red Monoazo Disperse Dyes

ICI *BP* 868,468 (4 Sept 1958)

The title dyes are prepared by coupling *NN*-bis(γ-chloro-β-hydroxypropyl, or γ-bromo-β-hydroxypropyl, or epoxypropyl) derivatives of benzene- or naphthalene-series amines with diazotised benzene-series amines free from NO_2, SO_3H, and COOH groups but containing such substituents as Hal, CN, $CONH_2$, SO_2Alk, $SO_2{\cdot}NH_2$, etc. Thus 2-chloro-4-ethylsulphonylaniline diazotised and coupled with *NN*-bis(γ-chloro-β-hydroxypropyl)-*m*-toluidine gives

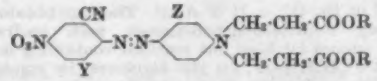


which dyes cellulose acetate and nylon scarlet. E.S.

Red and Violet Monoazo Disperse Dyes

ICI *BP* 865,328 (23 Dec 1958)

Monoazo compounds

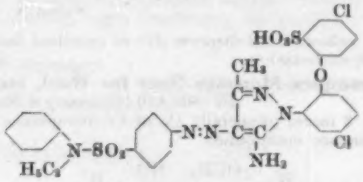


(R = Alk or hydroxyalkyl of < 6 C; Y = H or Hal; Z = H, Hal, or Alk of < 6 C) dye cellulose acetate and polyester fibres red and violet of good fastness to light and heat treatments. The coupling components are prepared by condensing suitable primary arylamines with acrylic esters $CH_2{:}CH{\cdot}COOR$. Thus diazotised 2-amino-5-nitrobenzonitrile couples with *NN*-bis-(β-carbethoxyethyl)-*m*-toluidine (Y = H; R = C_2H_5; Z = CH_3) to give a reddish violet. E.S.

Monoazo Pyrazole Acid Dyes

Gy *BP* 868,474 (Switzerland 3 Mar 1959)

Dyes similar to those of *BP* 844,427 are prepared by diazotising aniline having in the 3- or 4-position a group SO_2R (R = a possibly substituted hydrocarbon radical, OAr, or the radical of a secondary amine of > 3 C) and coupling with a 5-amino-1-arylpyrazolone preferably containing an SO_3H group. Thus diazotised aniline-4-sulphon-*N*-ethyl-*N*-phenylamide is diazotised and coupled with 5 - amino - 1 - (3′- chloro - 6′- (4″- chloro - 2″- sulphophenoxy-phenyl)-3-methylpyrazole to give

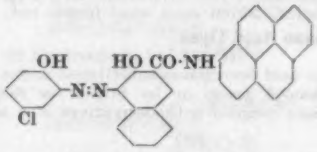


which dyes wool pure yellow from a neutral or weakly acid bath. E.S.

Metal-complex Monoazo Pigments

Ciba *BP* 864,896 (Switzerland 27 Apr 1956)

The title products are Co, Ni, Cu, or Cr complexes of *oo*′-dihydroxy- or *o*-carboxy-*o*′-hydroxy-monoazo compounds containing a group $-CO{\cdot}NH{\cdot}T$ (T = a radical containing at least 3 aryl ring systems, which may be heterocyclic). Thus the monoazo compound 2-amino-4-chlorophenol → 3-hydroxy-2-naphthoic acid is converted to the acid chloride, which is condensed with 3-aminopyrene to give the arylamide



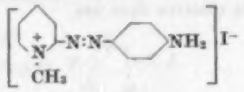
Heating in *o*-dichlorobenzene with stearato-chromium chloride gives the Cr-complex, which colours polyvinyl chloride grey-blue. E.S.

Basic Monoazo Dyes having a Pyridine Nucleus

American Cyanamid Co. *BP* 866,087 (U.S.A. 1 Mar 1957)

Polyacrylonitrile fibres are dyed bright red by aryl azopyridinium compounds prepared by condensing 2 (or 4)-halogenopyridines with nitroarylhydrazines, oxidising to the azo compound, reducing the nitro group to NH_2, and converting into the pyridinium quaternary salt. Thus 2-bromopyridine is condensed with *p*-nitrophenylhydrazine, the product oxidised with air and the

nitro group reduced by means of Na_2S. Treatment with CH_3I then gives the dye

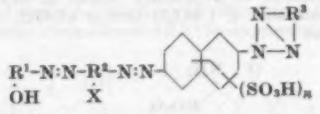


E.S.

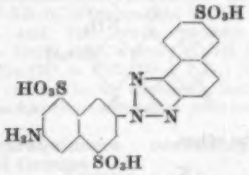
Green Metal(Copper and Nickel)-complex Disazo Direct Dyes having Triazole Rings

FBy *BP* 866,386 (Germany 23 July 1957)

The title dyes are Cu or Ni complexes of disazo compounds



(R^1 = radical of *o*-coupling hydroxy compound; R^2 = radical of benzene or naphthalene series in which the azo links are *para* to each other; X = chelatable group in the *o*-position to the external azo link; R^3 = radical of a naphthylamine, the N atoms being *ortho* to one another; n = 1 or 2). Thus the monoazo compound 6-nitro-2-naphthylamine-4,8-disulphonic acid → 2-naphthylamine-6-sulphonic acid is converted into the triazole, and the nitro group then reduced to give



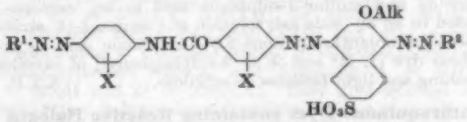
This is diazotised and coupled with 2-ethoxy-1-naphthylamine-6-sulphonic acid, and the aminoazo compound so formed is diazotised and coupled with R acid. Treatment with Cu salts then gives the green Cu-complex direct dye.

E.S.

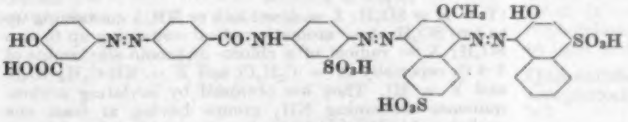
Green Metal(Copper)-complex Trisazo Direct Dyes

Fran *BP* 866,443 (France 16 Nov 1957)

The title dyes are 1:1 complexes prepared by coppering *o*-hydroxy-*o'*-alkoxyazo compounds



(R^1 = residue of salicylic acid; R^2 = residue of an *o*-coupling α- or β-naphtholmonosulphonic acid or acylamino-1-naphtholsulphonic acid; X = H, or one X may be SO_3H). As the salicylic acid residue is generally also metallised during coppering, a treatment with a metal-sequestering agent is required to obtain the required solubility and brightness of the finished dye. Thus the trisazo compound



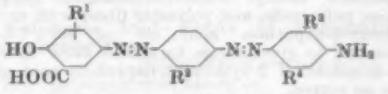
is heated for 12 h at 90–92°C with ammoniacal $CuSO_4$ and the complex is then partially decoppered by heating at 80–85°C with 1% aq. tetrasodium ethylenediaminetetra-acetate.

E.S.

Black Metallisable Tetrakisazo Direct Dyes

FBy *BP* 865,748 (Germany 12 Aug 1958)

The title dyes are prepared by acid-coupling diazotised 7-aminobenzotriazole (which may have a CH_3 group in the benzene nucleus) with J acid, and then alkali-coupling the monoazo compound so formed with the diazo compound of an aminodisazo compound



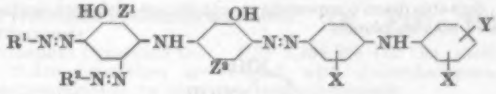
(R^1 = H or CH_3; R^2 = H or SO_3H; R^3 = OCH_3 or COOH; R^4 = H, CH_3, or OCH_3; when R^2 = SO_3H, R^3 = OCH_3). Thus reduction of the nitro group in the monoazo compound 5-nitro-orthanilic acid → salicylic acid gives an aminomonoazo compound which is diazotised and coupled with *p*-cresidine to give an aminodisazo compound. This is diazotised and alkali-coupled with the acid-coupled monoazo compound 7-aminobenzotriazole → J acid, to give the tetrakisazo compound which dyes cotton bluish black by the aftercoppering process.

E.S.

Brown Polyazo Dyes for Leather

FH *BP* 868,856 (Germany 28 Nov 1956)

3,3'-Dihydroxydiphenylamine is coupled with at least 1 mol. of a diazotised aminodiphenylaminesulphonic acid which may contain NO_2 or $NH{\cdot}CO{\cdot}CH_3$ groups and, if desired, up to 4 mol. of any diazo compound to give compounds



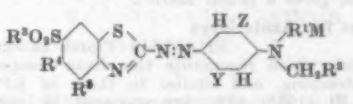
(one X = H, the other X = SO_3H; Y = H, NO_2 or $NH{\cdot}CO{\cdot}CH_3$; Z^1 = H or $-N{:}N{\cdot}R^3$; Z^2 = H or $-N{:}N{\cdot}R^4$; R^1, R^2, R^3, and R^4 = aryl radicals) which are of good solubility, and exhaust well on to leather in presence of even small quantities of acid and are thus suitable for brush dyeing. Thus diazotised 4-amino-4'-nitrodiphenylamine-2'-sulphonic acid is alkali-coupled with 3,3'-dihydroxydiphenylamine. A diazo solution from 2 mol. of aniline is then added, to give the yellowish brown trisazo dye.

E.S.

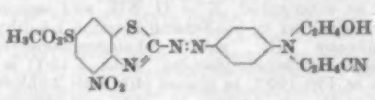
Benzothiazole-azobenzene and -azoquinoline Dyes

S *BP* 868,037 (Switzerland 5 Feb 1958)

Brilliant red and violet disperse dyes of excellent fastness to light, washing, perspiration, gas-fumes and water; pigments for lacquers, oils, synthetic resins and spin-dyeing of cellulose acetate; and, where an SO_3H group is present, dyes for wool, polyamides, polyacrylonitrile and animalised cellulosic fibres are



(R^1 = alkylene of 1–4 C; R^2 = hydroxyalkyl, dihydroxyalkyl, alkoxyalkyl, acetoxyalkyl, cyanoalkyl, CHF_2, CF_3, carbalkoxyalkyl or carbamoyloxyalkyl; R^3 = Alk or alkenyl, subst. or unsubst. NH_2; R^4 = H or Alk; R^5 = Hal, NO_2 or SO_3H; M = H, OH, alkoxy, acetoxy or carbamoyloxy; Y = H, Hal, Alk, alkoxy, CF_3, $NHCOCF_3$ or alkanoylamino; Z = H, Hal, Alk, alkoxy, or together with $-NCH_2R_3$ and the benzene nucleus, a tetrahydroquinoline ring). The amines used as diazo components are obtained from the appropriate aminobenzothiazole unsubst. in the 4-position, by halogenating, nitrating or sulphonating, or from a 2-amino-6-SO_2Hal-4,5-disubst. benzothiazole by acylating on the NH_2 group and converting the 6-SO_2Hal to the sulphinic acid, and alkylating or condensing with amines. Thus



is a brilliant violet dye of excellent fastness on acetate. 156 Examples are given.

A.T.P.

Methyl 5-Fluoroanthranilate—Diazo Component for Azoic Dyes
FH *BP* 866,781 (Germany 20 June 1956)

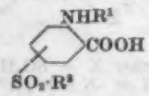
Diazotised methyl 5-fluoroanthranilate couples on cellulose, polyamide, and polyester fibres with arylides of 3-hydroxy-2-naphthoic acid (or of its 7-halogeno compounds) to give orange to scarlet azoic dyes. Thus the *o*-anisidide of 3-hydroxy-2-naphthoic acid gives an orange on cotton. E.S.

Azoic Coupling Components which React with Cellulose
BASF *BP* 865,305 (Germany 24 May 1958)

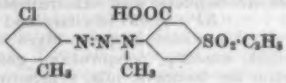
Coupling components containing at least one group $-SO_2\cdot N(R)A\cdot X$, $-SO_2N(A\cdot X)_2$, or preferably $-SO_2\cdot NH\cdot A\cdot X$ (R = H, Alk, Ar, etc.; A = alkylene of < 5 C and may contain OH; X = Hal) combine with cellulose under alkaline conditions and may then be coupled on the fibre with suitable diazo compounds. Sulphonic acid groups may be present in either component. Thus cotton is padded with a soln. in aq. NaOH of 1-naphthylamino-5-sulphon-β-chloroethylamide and then dried at 50–60°C and soaped. A thickened soln. of diazotised 2-naphthylamino-4,8-disulphonic acid is then applied to give a strong orange print of very good wet fastness. E.S.

Triazenes for Azoic Compositions
FBy *BP* 864,829 (Germany 9 July 1958)

Suitable diazo compounds are condensed with anthranilic acid alkylsulphones



(R^1 = subst. or unsubst. Alk; R^2 = Alk which may have substituents other than SO_3H and COOH) to give triazenes which regenerate the diazo compound readily and may thus be used in azoic printing compositions developable by neutral steaming. Thus diazotised 2-amino-4-chlorotoluene is condensed with 5-ethylsulphonyl-*N*-methylanthranilic acid to give



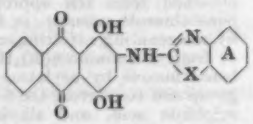
which, mixed with 3-hydroxy-2-naphtho-*o*-phenetidide, printed on cotton, dried, and steamed under neutral conditions, gives a bright scarlet. E.S.

Triazenes for Azoic Dyes
Fran *BP* 866,510 (France 11 June 1956)

Triazenes which regenerate the diazo compound on neutral steaming, and similar to those of *BP* 729,156 (*J.S.D.C.*, **71** (1955) 418), are prepared by condensing diazotised 2-amino-4,5-dichlorotoluene with *N*-(2-carboxyphenyl)glycine having at least 1 Hal substituent in the phenyl radical. E.S.

Anthraquinone Disperse Dyes
Ciba *BP* 867,791 (Switzerland 28 May 1957)

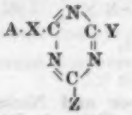
Brilliant pink disperse dyes of excellent fastness to light and sublimation on polyesters, and with good reserving of wool and cotton, are



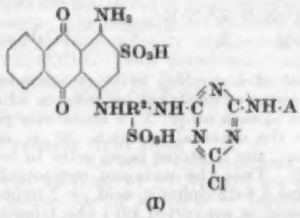
(A may be substituted; X = O, NH, and especially S). They are obtained by condensing 2-amino-1,4-dihydroxyanthraquinone (I) with 2-halogenobenzothiazoles, benzoxazoles or benzimidazoles. Thus, I (5·1) is heated for 24 h at 150–160°C in phenol (40) with 2-chlorobenzothiazole (4·1). On cooling to 70°C and diluting with ethanol (500), a brilliant pink dye of excellent light and sublimation fastness on Terylene is obtained. A.T.P.

Reactive Dyes for Cellulose—Anthraquinones containing Monohalogeno Triazine Residues
Ciba *BP* 867,571 (Switzerland 12 Sept 1956)

Water-soluble reactive dyes are

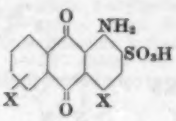


(A = anthraquinone dye residue containing < 1 SO_3H; X = $-N(C_{n-1}H_{2n-1})$; n = 1–3; Z = Hal; Y = residue of aromatic hydroxy sulphonic acid bound through its O atom, or residue of a primary mono- or bi-cyclic arylamine; Y contains < 1 SO_3H and/or COOH. Especially valuable are

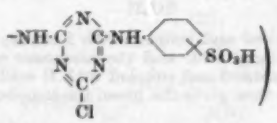


(I)

(R^2 = benzene residue; A = benzene sulphonic acid), and



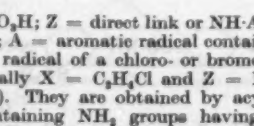
(one X = H, the other



They are prepared by known methods and dye synthetic-polymer fibres and especially cellulose (by the method of *BP* 798,121) in pure colours of excellent fastness to Cl_2, light and washing. Thus, the monocondensate of cyanuric chloride and aniline-3-sulphonic acid in aq. acetone is added to an aq. soda ash solution of 1-amino-4-(4′-aminophenylamino)anthraquinone-2,3′-disulphonic acid to give a blue dye (I, R^2 and A = 3-sulphophenyl) of excellent washing and light fastness on cellulose. A.T.P.

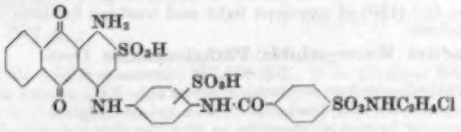
Anthraquinone Dyes containing Reactive Halogen
BASF *BP* 868,744 (Germany 31 Aug 1957)

These are



(Y = H or SO_3H; Z = direct link or NH·A containing up to two SO_3H; A = aromatic radical containing up to two SO_3H; X = radical of a chloro- or bromo-alkylamine of 2–4 C; especially X = C_2H_4Cl and Z = $NH\cdot C_6H_3\cdot SO_3H$ and Y = H). They are obtained by acylating anthraquinones containing NH_2 groups having at least one exchangeable H with arylcarboxylic acid halide sulphonic acid chloro- or bromo-alkylamides of up to 4 C in the alkylene radical. They dye animal fibres, polyamides, natural and regenerated cellulose very fast to light, washing and rubbing. Thus the condensate (10·6) of 1 mol. 1-amino-4-bromoanthraquinone 2-sulphonic acid and 1 mol. 1,4-diaminobenzenemonosulphonic acid is dissolved in H_2O (300) and treated at 0–5°C with benzoyl chloride-*p*-sulphonic acid-β-chloroethylamide (10) in acetone (30),

with continuous neutralisation of evolved HCl with 10% aq. Na_2CO_3. After stirring for 2–3 h at 5–10°C and salting out, a blue wool dye

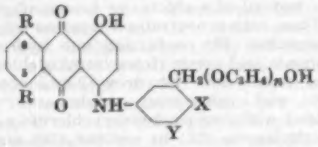


of excellent fastness is obtained in good yield. A.T.P.

Anthraquinone Blue Disperse Dyes

General Aniline *USP* 2,945,867 (30 Dec 1952)

1,8-Dihydroxy-4,5-dinitro- or 1,5-dihydroxy-4,8-dinitro-anthraquinone is condensed with the appropriate amine to give

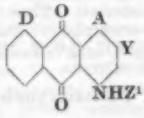


(one R = NO_2, the other OH; X = H, halogen or alkyl; Y = H or $CH_2(OC_2H_4)_nOH$; n = 1–3), violet, blue, and green disperse dyes of excellent fastness to light and gas fumes. Thus, 4,5-dinitrochrysazin (165) and 2,2′-(4-amino-2,6-tolylenedimethoxy)diethanol (281) are heated at 150°C for 7·5 h in nitrobenzene (1750). The mass is steam-distilled and the crude product filtered and extracted three times with warm CH_3OH (100) to give a greenish blue dye (R² = OH; R⁵ = NO_2; X = CH_3; Y = $CH_2OC_2H_4OH$; n = 1) of excellent fastness to light, washing and gas fumes on secondary cellulose acetate. A.T.P.

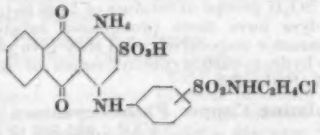
Arylaminoanthraquinones containing Halogeno-alkylsulphonyl Groups

BASF *BP* 868,743 (Germany 10 Sept 1957)

The above are



(A = H, NHZ^2 or preferably NH_2; Y = H or SO_3H; Z^1 = A·SO_2X, A $(SO_2X)_2$ or A (SO_2X) (SO_3H); D = H or NHZ^2; Z^2 = A·SO_2X, A$(SO_3H)_2$ or A(SO_2X) (SO_3H); A = aromatic radical free from COOH and ester groups and containing > 2 benzene nuclei; X = β or γ-chloro- or bromo-alkylamine residue, and especially A = NH_2; Y = SO_3H and Z^1 = A·SO_2X). They give dyeings on animal fibres, polyamides and cellulosic fibres of excellent fastness to light, washing and rubbing. They are obtained either by halogenating the analogous arylaminoanthraquinone-β- or γ-hydroxyalkylsulphones, or by condensing the appropriate arylaminoanthraquinone sulphonyl chloride with a β- or γ-halogenoalkylamine. Thus, 1-amino-4-anilinoanthraquinone-2-sulphonic acid (25) is treated at 20–25°C for 2 h and at 40–50°C for 2 h with $ClSO_3H$ (250), and the resulting sulphonyl chloride pasted with H_2O (150) and condensed with β-chloroethylamine hydrochloride (56) in H_2O (150) with addition of NaOH (7·2) and sodium acetate (14·8) in H_2O to give



a bright blue wool dye of excellent fastness. A.T.P.

1,1′-5,1″-Trianthrimide for Mass Coloration of Viscose Rayon

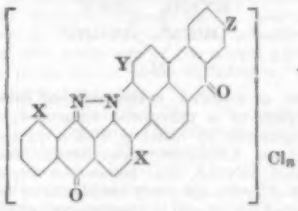
ICI *BP* 867,983 (14 Oct 1959)

1,1′-5,1″-Trianthrimide, used in the mass coloration of viscose rayon, yields maroons of extremely high fastness properties. It is preferable that ≮ 90% of the pigment particles should be < 3 μ in diameter and that the pigment should be free from anthraquinone compounds of low mol. wt. C.O.C.

Leuco Sulphuric Acid Esters of Benzanthrone-Pyrazolanthrone Dyes

FH *BP* 869,475 (Germany 9 Aug 1957)

The leuco sulphuric acid esters of

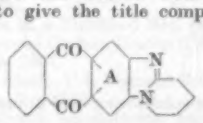


(one X = H, the other alkoxy of 1–4 C; Y = H, Alk of 1–5 C or phenyl; Z = H or Br; n = any value between 0 and 1) (prepared as in *GP* 1,000,383 and *GP* 1,025,880) are prepared in good yield by known methods. They are blue vat dyes of good affinity, excellent fastness to Cl_2, and high resistance to oxidation. A.T.P.

Pyridoimidazoloanthraquinone Vat Dyes and Pigments

American Cyanamid Co. *USP* 2,938,904 (12 Oct 1959)

2-Aminopyridines are heated with o-nitrohalogeno-anthraquinones to give the title compounds

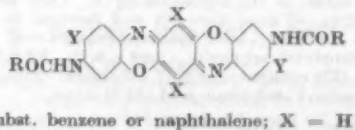


(CO groups linked with adjacent C atoms of A), orange vat dyes and pigments. Thus, 1-chloro-2-nitroanthraquinone (14·4) is refluxed for several hours with 2-aminopyridine (4·7) in glycol diacetate (100) in presence of sodium acetate (0·02). The product that separates on cooling is filtered, washed with ethyl acetate, and sublimed *in vacuo* to give an orange vat dye. A.T.P.

Dioxazine Pigments

Ciba *BP* 869,357 (Switzerland 29 May 1957)

Red to violet pigments of good heat stability, high fastness to light and migration are



(R = subst. benzene or naphthalene; X = H or Hal; Y = H, Hal, Alk or n-alkoxy). They are useful in "pigment printing", and for colouring lacquers, acetyl- and nitro-cellulose, resins, cosmetics, and as disperse dyes for synthetic-polymer fibres. E.g., 4-amino-2,5-diethoxy-1-nitrobenzene is condensed with chlorobenzoyl chloride and the NO_2 group reduced to give 4-(4′-chloro)benzamido-2,5-diethoxy-1-aminobenzene. This, with chloranil in alcohol, gives 2,5-dichloro-3,6-[2′,5′-diethoxy-4′-(4″-chloro)benzamido-phenylamino]-1,4-benzoquinone; cyclised with benzoyl chloride in nitrobenzene at 210–220°C it yields 2,6-di-(4′-chlorobenzamido)-3,7-diethoxy-9,10-dichloro-triphendioxazine, a violet pigment of excellent fastness to light and migration on polyvinyl chloride. A.T.P.

Quinacridone Pigments and 2,5-Bis-(arylamino)-terephthalic Esters as Intermediates therefor

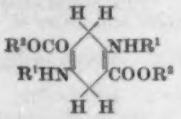
ICI *BP* 868,360 (6 June 1958)

Yellowish red to bluish red pigments of excellent fastness to light, heat, and solvents in paints, lacquers, and plastics are obtained by cyclising 2,5-bis(arylamine)terephthalic acids (or alkyl esters) with polyphosphoric acids at 120–190°C. Thus, 2,5-bis-phenylamino-terephthalic acid (15) is added during 20 min to tetraphosphoric acid (200) at 100°C and after heating to 150°C in 20 min, the mass is kept at that temperature until a test portion shows no alkali-soluble material, stirred into water (300) and

filtered (92% yield). The product (10) (as paste) is stirred with pine-oil (0·5) and dried at 40–50°C to give a bluish red pigment of excellent fastness.

BP 868,361 (4 Sept 1958)

3,6 - Dihydro - 2,5 - bis - (arylamino)terephthalic esters, having as one of their tautomeric forms

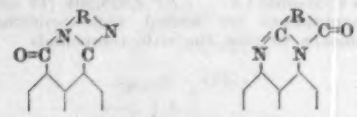


(R^1 = subst. or unsubst. carbocyclic or heterocyclic, or may form part of a polycyclic structure; R^2 = Alk) are dehydrogenated by heating with a quinone (e.g. 1,4-naphthoquinone, 2,6-dihydroxyanthraquinone, chloranil) in an organic solvent, e.g. monochlorobenzene. Thus, dimethyl-3,6-dihydro-2,5-bis-(phenylamino) terephthalate (1·9) is refluxed for 10 min in monochlorobenzene (20) with chloranil (1·25). Tetrachlorhydroquinone is filtered and the product (1·7) isolated by evaporation to dryness. These intermediates are obtained in high yield and good purity and are used in the manufacture of *lin*-quinacridone pigments. A.T.P.

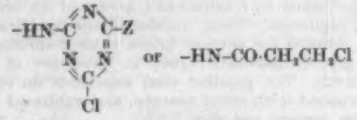
Reactive Perinone Dyes

Ciba *BP* 868,470 (Switzerland 18 Mar 1957)

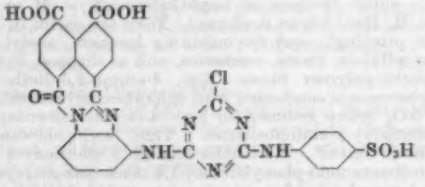
The above contain one of the groups



at least one water-solubilising acid group, and at least one residue of



(Z = etherified OH, subst. or unsubst. NH_2 or especially $-HN{\cdot}A{\cdot}SO_3H$; A = arylene, especially phenylene; R = aromatic residue). They may be obtained by reaction of a perinone containing at least one acylatable $-NH_2$ group with β-chloropropionyl chloride or a 2,4-dichloro-1,3,5-triazine subst. in the 6-position by Z. They are mainly yellow dyes, of good strength and fastness to light on cellulose. Thus, the monocondensate of 1,4,5,8-naphthalenetetracarboxylic acid and 1,2,3-triaminobenzene (37) condensed with 2,4-dichloro-6-phenylamino-1,3,5-triazine-4′-sulphonic acid (34·3) gives



a brownish yellow reactive dye for cotton and regenerated cellulose. A.T.P.

Water-soluble Phthalocyanine Dyes

BASF *BP* 868,747 (Germany 6 July 1957)

Phthalocyanine polysulphonic acid chlorides are reacted with primary or secondary hydroxyalkylamines (1–4 C) so that at least one $-SO_2Cl$ group is amidised and at least one unamidised. The residual $-SO_2Cl$ groups are saponified to SO_3H, and replacement of OH in the sulphonic acid hydroxyalkylamide group by Cl or Br gives the title compounds, blue dyes for cellulose of excellent fastness to light and washing, and greater solubility and fastness to boiling soda than the dyes derived by amidating all the SO_2Cl groups. Thus, ice (300) and hydroxyethylamine (11), and, over several hours, 15% aq. NaOH (140), are added to an aq. suspension (600) containing Cu phthalocyanine trisulphonyl chloride (100). After stirring for 15 h at room temperature, the dye is precipitated with HCl. It is refluxed in excess of $SOCl_2$ to give a brilliant blue dye (130) of excellent light and washing fastness on cellulose. A.T.P.

Reactive Water-soluble Phthalocyanine Dyes

BASF *BP* 868,746 (Germany 8 Nov 1957)

Phthalocyanines containing acylatable NH_2 groups are reacted with alkylcarboxylic acid halide sulphonic acid chloro- or bromo-alkylamides to give the title compounds, blue dyes of excellent fastness to light, washing, and rubbing for wool and cellulosic fibres. They are $(G)_z{\cdot}A{\cdot}(D)_y$ (A = phthalocyanine residue; D = $E{\cdot}NH{\cdot}CO{\cdot}A{\cdot}SO_2X$; G = SO_3H, $SO_2NH{\cdot}A{\cdot}SO_3H$, $SO_2NH{\cdot}A(OH){\cdot}SO_3H$ or $SO_2NH{\cdot}A(SO_3H)_2$; y = 1–4; z = 0–3; y + z = 1–4, E = direct link, $CH_2{\cdot}A{\cdot}(OH){\cdot}SO_3H$ or $SO_2NH{\cdot}A{\cdot}SO_3H$; A = aromatic radical of 1–2 benzene nuclei; X = radical of a chloro- or bromo-alkylamine of of 1–4 C). Thus, into a neutralised aqueous solution of a Cu phthalocyanine (30) containing one hydroxyaminobenzenesulphonic acid group (from tetrakis(chloromethyl) Cu phthalocyanine and 1-hydroxy-2-aminobenzene in monohydrate and subsequent sulphonation in 10% oleum) is added, with cooling, benzoyl chloride-*p*-sulphonic acid chloroethylamide (25) in acetone (50) and enough 10% aq. Na_2CO_3 to ensure pH < 7. After stirring for several hours at room temperature, KCl is added to precipitate a greenish blue dye (65) of excellent fastness to washing on cellulose. A.T.P.

Phthalocyanine Dyes

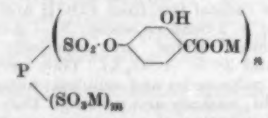
BASF *BP* 868,913 (Germany 10 May 1958)

Phthalocyanine sulphonic acid chlorides are reacted with amines substituted on the amino H by one or two ether groups, $-X{\cdot}O{\cdot}Y$ (I) (X = alkylene; Y = linear or branched Alk or cycloalkyl). They are used for colouring organic liquids, for air-drying, oven-drying or acid-hardening lacquers containing, e.g. nitrocellulose, synthetic resins, etc. They have greater solubility in organic solvents than analogous dyes containing OH, hydroxyalkyl, or cyclic ether groups in place of I, and they have less odour, thus making them more suitable for colouring foodstuff packing materials. Thus Cu phthalocyanine 3,3′,3‴- or 4,4′,4‴-trisulphonyl chloride is condensed with $(C_2H_5)(C_4H_9){\cdot}CH{\cdot}CH_2{\cdot}O{\cdot}C_2H_4{\cdot}NH_2$ to give a blue dye soluble in organic solvents. A.T.P.

Esters of Copper Phthalocyanine Tetrasulphonic Acids

DH *BP* 868,682 (Switzerland 27 Mar 1957)

3′-Hydroxy-4′-carboxyphenol esters of Cu phthalocyanine tetrasulphonic acids are



(P = Cu phthalocyanine residue; and the above substituents are present one in each of the 4 benzene nuclei of P and collectively in both the 3- and 4-positions of the phthalimides from which P is derived; m = 0–3; n = 1–4; m + n = 4; M = H, alkali-metal or NH_4). They are prepared from the corresponding phthalocyanine tetrasulphonyl halides (3,4′,4″,4‴ or 3,3′,4″,4‴ or 3,3′,3″,4‴) and 1–4 mol. of the requisite 1,3-hydroxybenzene-4-carboxylic acid (I). The dyes are for vegetable, animal or synthetic fibres and for anodised Al. Depending on whether SO_3H groups or residues of I are in preponderance, the dyes have more pronounced substantive or mordant character respectively and they give purer blues than the *o*-hydroxycarboxyphenyl esters of *BP* 768,444 (J.S.D.C., 73 (1957) 275). A.T.P.

Non-flocculating Copper Phthalocyanines

DuP *USP* 2,933,505 (5 Feb 1957)

Chlorine-containing Cu phthalocyanines are synthesised from *o*-arylene dinitriles (e.g. phthalonitrile) and a Cu chloride at 180–250°C in presence of 0·015–0·15 mol. aromatic tertiary nitrogenous base per mol. dinitrile, and mechanically ground. The products are flocculation resistant, crystal stable, and predominantly in the α-crystal

phase. If chemical methods are used for reducing particle size, flocculation resistance is destroyed. A.T.P.

Water-soluble Dyes containing Sulphuric Ester Groups
ICI *BP* 868,285 (9 July 1958)

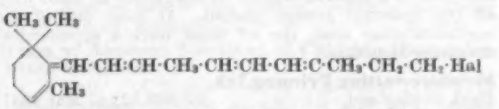
The above are

D–(–CH_2·X·Y·OSO_3H)$_m$

(D = coloured residue; X = S or N; Y = divalent cycloalkylene, alkylene, hydroxyalkylene, sulphatoalkylene, or allyloxyalkylene; m = 1–8. Where X = N, N carries an alicyclic or preferably H or aliphatic radical). The dyes may be polycyclic quinones, azo, azoxystilbene, acridine, thiazine, azine, di- and tri-arylamine, indigoid, peridicarboxylic imide, nitro- or phthalo-cyanine. They have excellent washing fastness on protein and synthetic fibres and especially on cellulose, and when applied to cellulose in conjunction with alkali give very fast dyeings, probably because of reaction with the fibre. Where D = a vattable residue, they are vat dyes of excellent fastness and are more easily reduced to the leuco compound than analogous dyes without the –CH_2·X·Y·OSO_3H group. Thus, Cu tris-(di-β-hydroxyethylaminomethyl)phthalocyanine (10) is heated at 90°C with pyridine (98) and $ClSO_3H$ (17·7) until a sample is soluble in 2-N Na_2CO_3, the mixture added to water (250) and a bright blue dye for cellulose precipitated by potassium acetate. Similarly, bis-(*N*-methyl-*N*-β-hydroxyethylaminomethyl)-isodibenzanthrone is sulphated with 98% H_2SO_4 to give a water-soluble violet vat dye. A.T.P.

β-Carotene (C.I. 75130)
Eastman Kodak Co. *USP* 2,945,069 (31 Jan 1958)

β-Carotene is synthesised by reacting retrovitamin A halide,



with a triaryl phosphone to form a retrovitamin A triaryl phosphonium halide. Treatment with a strong organic base converts this to a triarylphosphorous-ylid having the vitamin A carbon structure and this, when treated with vitamin A aldehyde, yields β-carotene. C.O.C.

Stabilised Aluminium Paste Pigments
English Metal Powder Co. *BP* 869,957 (26 Aug 1958)

Aluminium paste pigments containing a little *o*-cresol retain their leafing power indefinitely under normal conditions of storage and transport. Some of the *o*-cresol may be replaced by *p*-toluidine. C.O.C.

Alumina–Silica Pigment for Rubber and Paper
Columbia–Southern Chemical Corpn. *USP* 2,943,948 (24 June 1959)

White alumina–silica pigments containing $\leq$ 6 moles of SiO_2 per mole of Al_2O_3, when of particle size 0·01–0·05 μ, are suitable for use in rubber compositions and, when of particle size 0·05–0·25 μ, for use with paper. C.O.C.

Dark Blue Nacreous Molybdenum Disulphide
Francis Earle Labs. *USP* 2,945,770 (4 Dec 1957)

A dark blue, nacreous pigment is obtained by heating at high temperature (preferably red heat) a mixture of MoO_3 and S in any desired proportion in a covered vessel. The product is finally air-quenched, cooled and dispersed by heating in water. After filtration and washing, rod-like crystals, 1–30 μ long and up to 12 μ thick are obtained. The thickness of the crystals is not a material factor in determining their nacre-producing ability so long as they are thick enough to be opaque, a thickness of 1 μ or less being usually sufficient. C.O.C.

Siliceous Pigments for Paper
Columbia-Southern Chemical Corpn. *USP* 2,943,970 (14 Apr 1959)

Flocculated, amorphous siliceous pigments of ultimate particle size < 0·25 μ and in which at least 55% of the fibres are of particle size 0·5–7·0 μ are very effective for improving the opacity and brightness of paper. C.O.C.

Silica (C.I. Pigment White 27)
Columbia-Southern Chemical Corpn. *USP* 2,946,660 (1 Nov 1957)

Acid-precipitated silica containing cationic impurities is purified by making it into an aqueous slurry, establishing therein 0·02–0·50 g of a metal salt per litre of slurry, and treating with an ion-exchanger. C.O.C.

Titanium Dioxide (C.I. Pigment White 6)
Laporte Titanium *BP* 866,363 (31 Jan 1958)

A titanium tetrahalide is treated with oxygen in a fluidised bed of refractory material at 750–1500°C. At least some of the TiO_2 remains in the bed. The size distribution of the bed's particles is controlled by adding from outside fluidisable particles of alumina, silica, zirconia, zircon or TiO_2. Particles are gradually withdrawn from the bed, the mean size of the added particles being less than the mean size of those withdrawn. C.O.C.

Self-luminous Substances
Westo G.m.b.H. Fabrik für Chemische-technische Erzeugnisse and Gamma Gesellschaft für Praktische Radiologie Hartmann & Futterknecht *BP* 869,698 (Germany 12 Oct 1957)

A self-luminous substance, e.g. Zn-Cd sulphide, is stimulated into luminescence by a layer consisting of tritium absorbed on a metal, preferably Ti or Zr. As no fast β- or γ-rays are given off there is no need for a special absorbing layer for such rays. C.O.C.

Phosphorescent Material
H.M. Postmaster-General *BP* 870,504 (26 Feb 1958)

HCHO is combined with a substance with which it forms a solid condensate and with an activating non-phosphorescent substance, e.g. amino G acid or *p*-phenylphenol solution. The product is strongly phosphorescent. C.O.C.

Washing Pigments in a Fluidised Bed (I p. 373)
Structure of Dispersed Carbon Blacks (C.I. Pigment Black 6 and 7) (V p. 388)
Oxidised Carbon Black (C.I. Pigment Black 6 and 7) for Printing Inks (V p. 388)
The Relation Between Constitution and "Accumulating Power" of Brightening Agents in Washing Treatments with Anionic and Non-Ionic Detergents (VII p. 390)
Dyeing Cellulose with Reactive Dyes containing Arylurethane Groups (VIII p. 391).
Dyes for Polyethylene Terephthalate (VIII p. 391)
Dyeings of Good Fastness to Perspiration on Leather by Use of Azo Dyes containing Phosphonic Acid Groups (VIII p. 391)
Photoactivation of Aminotriarylmethane Dye Cyanides (IX p. 392)

V— PAINTS; ENAMELS; INKS

Theory of Drying of Drying Oils
J. P. Helme, J. Molines, G. Bosshard, and M. Rouzier *Peintures, pigments, vernis*, **36** (1960) 574–587

Autoxidation of methyl esters of linseed oil fatty acids proceeds through formation of hydroperoxides which decompose to yield various products, e.g. unsatd. αβ-ketones, hydroxides, dihydroxides, epoxides, dihydroxyketones, and diketones. Finally these products decompose and form, in part, polymers. A free-radical mechanism for chain formation is envisaged, and C–C as well as C–O bonds appear to be formed. C.O.C.

Study of the Thixotropic Properties of Structural Colloid Systems and their Utilisation in the Study of Varnish and Dye Materials
T. A. Amfiteatrova *Lakokrasochnye Materialy i ikh Primenie*, (4) (1960) 58–63
Chem. Abs., **55** (3 Apr 1961) 6881

Review, 35 references. C.O.C.

Zinc Dust (C.I. Pigment Metal 6) Paints
Paint (India), **9** (4) (1959) 29–31
Chem. Abs., **55** (20 Mar 1961) 5983

Review, 100 references. C.O.C.

Ageing of Paints and the Critical Pigment Volume Concentration (CPVC)
B. Svoboda and J. Kořínský *Farbe u. Lack*, **66** (1960) 385–393

The CPVC of linseed oil paints increases with the degree of pigment dispersion. Equilibrium between

adsorption and agglomeration is reached during storage. Appreciable increase in CPVC occurs in systems of low acid number. Addition of linseed oil fatty acids gives a higher initial CPVC, which remains relatively constant. Addition of Zn naphthenate increases and of water decreases CPVC. Optimum gloss and hardness are obtained at maximum CPVC. C.O.C.

Paint Materials, Protective Agents, and Impregnations on Urethane Bases in conjunction with Castor Polyols
T. C. Patton *Deutsche Farben-Zeitschrift*, **15**, (May 1961) 198–206

The preparation and uses of urethane coatings on castor polyols are described and discussed (cf. also A Survey of Urethane Coatings, *Paint Industry Mag.*, Sept. 1959). These protective coatings have already secured a permanent place in the American lacquer industry because of their flexibility, hardness, resistance to chemical solvents and rubbing, and durability. The chemistry of the principal urethane involved—toluylene di-isocyanate—is surveyed, together with the various carriers employed, and the one- or two-component systems which arise. The many uses of urethane paints are mentioned. There are 6 tables of data and 25 references. H.H.H.

Colloidal and Chemical Principles of Changes in Optical Properties and in Atmospheric Stability of Lacquer Films Containing Carbon Black
Ya. M. Gurevich and R. F. Minaeva *Kolloid. zhur.*, **22** (Nov–Dec 1960) 658–662

The influence of colloidal and chemical processes occurring during drying on the optical properties of lacquer films containing Carbon Black pigments has been investigated. The effects of water, heat, and light have been also examined. Lustre and brightness of lacquer films are determined by the degree of aggregation of pigment particles. Changes in lustre and brightness observed during exposure to light in warm water were brought about by the presence in the adsorption layers of films of particles with increased activity capable of initiating and catalysing oxidation reaction. Lacquer films which show decreased tendency to oxidation and therefore are more resistant to exposure to light have been prepared. L.S.L.

Structure of Dispersed Carbon Blacks (C.I. Pigment Black 6 and 7)
A. Voet and W. N. Whitten *Rubber Age*, **86** (1960) 811–818 *Chem. Abs.*, **55** (20 Mar 1961) 5805

Analysis of the structural involvement of several commercial Carbon Blacks dispersed in white mineral oil was made by measuring the D.C. conductivity and dielectric constant in quiescent and sheared dispersions at several concentrations and temperatures. Whether they are dispersed in gases, liquids or elastomers, the structural involvement of Carbon Blacks is the result of an interplay of attractive and repulsive forces between individual particles. It is possible to classify Carbon Blacks by this method. C.O.C.

Oxidised Carbon Black (C.I. Pigment Black 6 and 7) for Printing Inks
T. N. Malova and V. I. Romanova *Sbornik Nauch. Rabot. Vsesoyuz. Nauch.-Issledovatel. Inst. Poligraf. Prom.*, (8) (1958) 94–100 *Referat. Zhur., Khim.*, (1959) Abstr. No. 76878 *Chem. Abs.*, **55** (20 Mar 1961) 5984

Study of the effect of Carbon Blacks of different degrees of oxidation and different specific surface areas on the viscoelastic properties, rate of drying, and intensity and mobility of inks during drying. Oxidation of Carbon Black leads to a 3–4-fold increase in specific surface; however, there is not always a direct relation between the content of volatile components and the specific surface area. The dispersity of Carbon Black is not altered by oxidation. Oxidised Carbon Blacks have increased moisture content and their oil content is approximately twice that of the original pigments. They have a lower maximum shearing stress. The mobility of the inks depends upon the coefficient of mobility (ratio of maximum shearing stress, θ, to the viscosity, η); for well-circulating inks it is > 1. Oxidised Carbon Blacks have good mobility because of their high viscosity and low θ value. Their principal defects are their antioxidant and highly hygroscopic properties. Tests made by printing illustrations with oxidised Carbon Blacks showed that the optimum content of volatile components in the pigments is 13–16%. C.O.C.

Influence of Structural and Mechanical Properties of Printing Inks on their Behaviour during Printing
T. I. Gudkova, L. A. Kozarovitskii and N. V. Mikhailov *Kolloid. zhur.*, **22** (Nov–Dec, 1960) 649–657

The behaviour of printing inks under conditions corresponding to those encountered during printing, where the printing paste is subjected to a velocity gradient greater than 10^4 sec^{-1}, have been studied. A structural breakdown with large decrease in viscosity of the paste occurs. Complete rheological curves of velocity gradient against shearing stress have been obtained. The main rheological characteristics of the paste which determine behaviour in printing are (*a*) the relation between original and final viscosities (η_0/η_f), (*b*) the pressure range over which the decrease in viscosity occurs, and (*c*) the kinetics of thixotropic regeneration of structure. During actual printing, the main rheological factor is the constant minimum viscosity of the paste. Increase in temp. from 20 to 50°C decreases minimum viscosity nearly five-fold. Further temp. increase (to 80°C) has little effect on viscosity. The amount of paste transferred to the paper is inversely proportional to η_f (final viscosity). L.S.L.

PATENTS

Thixotropic Oils
FBy *BP* 867,772 (Germany 21 Oct 1958)

An oil (1 mol.) is inter-esterified in presence of a catalyst with a polyhydric alcohol (0·5–2·5) and then treated with sufficient of a masked organic di-isocyanate to react with all the hydroxyl groups present. At least one of the reactants other than the oil must have a symmetrical molecular structure. C.O.C.

Moisture-setting Printing Ink
Bank of England *BP* 868,122 (7 Mar 1957)

A moisture-setting ink having good chemical resistance is obtained by dispersing a pigment in a mixture in a glycol solvent of (*a*) either a water-insoluble novolak resin formed from phenol or cresol and HCHO or a water-insoluble condensed cyclohexanone resin, and (*b*) a water-insoluble alkyd resin modified with a drying or semi-drying oil. C.O.C.

Non-printing Indicia Ink
Sperry Rand Corpn. *USP* 2,936,241 (16 May 1957)

An ink suitable for use as a non-printing indicia medium on offset printing plates of the colloid type, i.e. it preserves the hydrophilic nature of the plate in the area of indicia printing, comprises a hydrophilic plasticiser, a film former, an inorganic pigment or water-soluble organic dye and a mild base which is insoluble in neutral or alkaline medium. An example is glycerol (25–35%), dextrin (10–20), TiO_2 (C.I. Pigment White 6) (0–15), Ultramarine Blue (C.I. Pigment Blue 29) (10–30), $CaCO_3$ (C.I. Pigment White 18) (5–25) and China Clay (C.I. Pigment White 19) (0–20). C.O.C.

Watercolour Paint Compositions that absorb Ultraviolet Radiation
Printing Arts Research Labs. *USP* 2,944,912 (31 July 1958)

Paints that absorb ultraviolet radiation are produced by including in the paint an absorber of ultraviolet radiation dissolved or dispersed in a water-soluble or -dispersible, oil- or wax-like material which functions as an exudation agent and carrier for the absorber. The exudation agent, which is preferably a polyethylene glycol, is dissolved or dispersed in the aqueous-base of the paint while the paint is liquid, but when the paint is dried it exudes to the paint film surface carrying the absorber with it, so that the absorber completely coats the pigment particles. C.O.C.

Rapidly Hardenable Mixtures of Epoxy Resins and Polyamide Resins
Ciba *BP* 864,357 (Switzerland 2 Oct 1956)

Use of Mannich bases of formula $R^1(CH_2N(R^2)_2)X$ ($X > 1$; R^1 = mono- or poly-nuclear mono- or poly-phenol containing X free valencies; R^2 = Alk or hydroalkyl or the two R^2 radicals together with the N atom form

a ring), e.g. 2,4,6-tri-(dimethylaminomethyl)phenol, accelerates the hardening period without detracting from the desirable properties of the polyamide resin as the primary curing agent. C.O.C.

Reflective Coating Compositions
Minnesota Mining & Manufacturing Co.
BP 867,783 (U.S.A. 14 June 1956)

A liquid composition which on application to a substrate and drying becomes immediately reflex-reflecting comprises a varnish, metal-flake reflective pigment, and transparent microspheres of glass of refractive index $< 1{\cdot}8$. The pigment particles must be substantially smaller in size than the microspheres. C.O.C.

Solvent for Vinyl Chloride–Vinyl Acetate Copolymers (III p. 377)
Removal of Organic Coatings (XIII p. 396)
Protecting Halogen-containing Polyester Resins against Outdoor Exposure (XIII p. 397)

VI—FIBRES; YARNS; FABRICS

Bonded Fibres
Chem. and Ind., No. 16 (22 Apr 1961) 487–492

A brief account of the symposium organised by the S.C.I., the S.D.C. and the T.I. and held on 20th Oct 1960. The papers cover bonded fabrics, bonding in paper sheets, and the use of glass fibres in plastics. P.B.S.

Fibre Modification by Irradiation and Polymer Grafting
A. J. Hall *Text. Rec.*, **79** (May 1961) 57–59

Progress in the modification of textile fibres by high-energy irradiation is discussed and some examples are given. Possible uses of this method, including increasing dye receptivity, are indicated. W.R.M.

Action of Aqueous Solutions of Chlorine Dioxide on Cotton Cellulose
T. P. Nevell *J. Textile Inst.*, **52** (Apr 1961) T185–T194

Molar sodium chlorite at pH 2·9 and 20°C causes oxidation of hydrocellulose, in addition to converting terminal reducing groups to carboxyl groups. Unmodified cotton cellulose behaves similarly after an induction period of about 24 h. It is believed that oxidation is due to chlorine dioxide. Aqueous solutions of chlorine dioxide at 20°C oxidise cotton cellulose. The rate of oxidation increases with increasing concentration of chlorine dioxide and with increasing pH. Oxidation appears to occur in two stages—the formation of reducing groups and their conversion to carboxyl groups. The first stage is accelerated by increasing pH, but the second occurs more rapidly at pH $\leqslant 5$ than at pH 6. The relationship between fall of copper number and rise in carboxyl content is independent of the pH of the chlorine dioxide solution, suggesting that the nature of the primary oxidation is also independent of this pH. W.R.M.

Studies in Fellmongering. II—Influence of Curing and Soaking Conditions and of Temperature of Sweating
G. H. Green *J. Soc. Leather Trades Chem.*, **45** (Apr 1961) 167–174

Complete loosening of wool is considerably accelerated within the range 10–20°C but rather less so over the range 20–35°C, and 25–35% of the skin N is solubilised, whatever the temp. This is less than the estimated non-collagenous N based on hydroxyproline determination; this and other evidence suggests that under normal conditions, no appreciable attack on the collagen necessarily occurs. J.W.D.

Electron Microscopic Structure of Collagen
K. Hess *Melliand Textilber.*, **42** (Mar 1961) 305–309

X-Ray photography and electron microscopy revealed the existence of periodically repeated transverse striations in different types of fibres (collagen, polyamide, polyvinyl alcohol, natural and regenerated cellulose). Chemical constitution cannot be responsible for this phenomenon. It must be due to physical factors and it is suggested that the striations are caused by periodic alternation of ordered and disordered regions in the fibre. The periodicity can be explained by thermodynamical reasoning which even permits calculation of the experimentally measured values of the periods. W.M.

Morphology of the Cuticle Layer in Wool Fibres and Other Animal Hairs
M. G. Dobb, F. R. Johnston, J. A. Nott, L. Oster, J. Sikorski, and W. S. Simpson
J. Textile Inst., **52** (Apr 1961) T153–T170

Electron microscopy studies are used to obtain information regarding the morphology of cuticle cells. An idealised model can account for two distinct mechanisms of deformation of fibres. Evidence is obtained supporting "ploughing" action during motion in the tip-to-root direction. W.R.M.

Synthetic Fibres
P.-A. Koch *Textil-Rund.*, **16** (Mar 1961) 117–125

A concise summary of the preparation and properties of synthetic-polymer fibres (Fibre Table No. 9). P.B.S.

Acrylic Fibres
J. W. S. Hearle *Text. Manuf.*, **87** (Apr 1961) 131–135

The constitution, production, structure, physical and chemical properties of the various acrylic fibres (containing at least 85% of polyacrylonitrile) are outlined and some of the main end-uses indicated. S.B.D.

Polyamide Fibres—I
P.-A. Koch *Tinctoria*, **58** (Mar 1961) 94–106

Lists trade names, history of discovery, raw materials, methods of manufacture, chemical constitution, technological data, physical properties, and chemical resistance. Affinity for different classes of dye is briefly mentioned and methods to distinguish between nylon 6 and nylon 6.6 are given. Advantages and disadvantages of polyamide fibres and the fields in which they are used are surveyed. 229 References. W.M.

PATENTS

Matt Cellulose Ester Fibres
Wacker-Chemie and CFM
BP 866,508 (Germany 16 May 1956)

Addition of a melamine–formaldehyde condensate to a cellulose acetate solution, followed by treatment of fibres formed from the solution with hot air, hot water, or steam imparts to the fibres a wool-like matt appearance without impairing their colour, physical properties, or resistance to degradation by light. C.O.C.

Regenerated Protein Fibres
Textile & Chemical Research Co.
BP 867,935 (France 17 Dec 1958)

Addition to an aqueous composition of protein material of a small amount of carboxymethylcellulose imparts to fibres formed from the composition increased ability to react with HCHO to form an insoluble three-dimensional structure. The resulting fibres have much better wet strength than fibres formed from compositions containing no carboxymethylcellulose. C.O.C.

Polyester Fibres Having Good Affinity for Metallisable Dyes
Eastman Kodak Co. *USP* 2,945,010 (24 Oct 1956)

A nuclearly substituted amino aromatic non-metallised compound containing 6–20 C, e.g. *NN'*-diphenylethylenediamine, is mixed with the polyester before it is extruded. After extrusion the fibres are treated with a boiling solution of a water-soluble mordant salt, e.g. treatment for 1 h with a 5% aqueous solution of Ni thiocyanate yields a fibre which dyes readily with Ni chelate dyes. C.O.C.

Antistatic Finish for Fibre-forming Linear Polymers
Vereinigte Glanzstoff Fabriken
BP 862,963 (Germany 16 June 1956)

Addition to the monomer or the polymer of 0·01–2·0% by weight of a compound of formula $R_3A{\cdot}AR_3$ (A = Sn or Ge; R = naphthyl, phenyl, halogenated or alkylated phenyl, or cyclohexyl), e.g. hexaphenyl distannane, and hexacyclohexane digermanane, imparts an antistatic finish which neither yellows nor is washed out during processing nor affects any of the equipment used during processing. C.O.C.

1,1′-5,1″-Trianthrimide for Mass Coloration of Viscose Rayon (IV p. 385)
Infrared Spectroscopy in the Study of the Reaction of Cellulose with Basic Dyes and Metals (VIII p. 390)
Role of Spiral Structure in Untreated and Treated Cottons (X p. 393)

Grafting of Cellulose Acetate (X p. 394)
Bonded-fibre Fabric (X p. 395)
Relationship between Alkali Solubility and Percentage of Short Chains in Native and Regenerated Celluloses (XI p. 395)
Cross-linking of Polyvinyl Alcohol (XIII p. 397)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Combined Hydrogen Peroxide–Hypochlorite Method of Bleaching Linen

A. M. Bolobonov, E. A. Barashkova, and A. A. Slitkova

Tekstil. prom., No. 10 (Oct 1960) 58–59

Typical linen fabrics are bleached, after desizing and scouring, by preparing in sodium hypochlorite and mangling straight into hydrogen peroxide without intermediate washing; the active chlorine content of the padded fabric must not exceed 0·1% of air-dried wt. The advantages claimed over the older hypochlorite bleaches are reduction in time, chemicals, and power consumed, together with a higher degree of whiteness and less tendering. G.J.K.

The Relation Between Constitution and "Accumulating Power" of Brightening Agents in Washing Treatments with Anionic and Non-ionic Detergents

H. Häusermann and R. Keller

Textil-Rund., **16** (Apr 1961) 176–180

In repeated washing treatments with detergents containing brightening agents the brightening effect on the washed material increases continuously. This phenomenon is called "accumulation" and is influenced by temperature, pH, liquor ratio, etc., and especially by the ionic character of the detergent. A series of derivatives of 4,4′ - bis[1″,3″,5″ - triazinyl - (6) - amino]stilbene - 2,2′ - disulphonic acid is used to show the effect of different substituents upon the "accumulating power". The percentage difference in the accumulated brightening effect (measured fluorometrically) between anionic and non-ionic washing is used to compare the "accumulating powers" of different compounds. Polar groups in the brightening agent increase the "accumulating power" strongly whilst non-polar groups reduce it. The paper is mainly concerned with soluble brightening agents applicable to cotton and nylon, but a brief account of four insoluble agents for synthetic-polymer fibres is given. P.B.S.

PATENTS

Continuous Chlorite Bleaching

M. Stoffel *BP* 864,230 (Switzerland 19 Sept 1956)

The material is impregnated with an inactive alkaline or neutral alkali-metal chlorite solution containing a potentially acid salt, e.g. NH_4Cl or $(NH_4)_2SO_4$, and then heated so that the solution is acidified and activated by decomposition of the salt. C.O.C.

Treating Petroleum-based Dry-cleaning Solvent with Diglycollic Acid to Remove Smell

Emery Industries *USP* 2,944,964 (24 Dec 1958)

The odour of perspiration is removed from the solvent by distilling it and then treating with diglycollic acid, e.g. by passing through a "rag drier", the rags of which are impregnated with acid which is not miscible with the solvent. C.O.C.

VIII— DYEING

Reduction of Indigo in Fermentation Vats

Y. Takahara and O. Tanabe

I— Fermentation Process

Hakko Kogaku Zasshi, **38** (1960) 176–180

Acid was produced during fermentation and the oxidation–reduction potential of the vat gradually decreased to reach finally −700 mv. By the time fermentation became visible, growth of the bacteria responsible for it had almost ceased and the oxidation–reduction potential had greatly decreased. Continuous neutralisation to preserve a high pH is necessary, as fermentation proceeds most smoothly in alkaline conditions.

II— Factors Influencing Fermentation

Ibid., 180–183

Chem. Abs., **55** (3 Apr 1961) 6776

The vat is preferably set with a 5% solids content. To keep reduction proceeding smoothly and to prevent microbial contamination it is necessary to maintain pH 10–12. Optimum temperature is 30°C but good results are obtained at 20–40°C. C.O.C.

Use of Sodium Bicarbonate in Package Vat-dyeing of Cotton Yarn

H. Borsten *Tex*, **20** (Mar 1961) 111–117

Addition of sodium bicarbonate in the final stage of vat dyeing, before oxidation, increases the depth of the dyeing. Though most effective with IW-dyes, the method can also be used with IN-dyes, but does not work with IK-dyes. The bicarbonate treatment need not result in any serious deterioration of rubbing fastness or of uniformity of dyeing. It is, however, essential that addition is rapid, preferably taking not longer than 3 min. Experiments indicate that the addition of bicarbonate can lead to appreciable savings in dyeing costs. The method can also be used in the dyeing of piece goods on the jig and in continuous vat-dyeing. R.A.

Infrared Spectroscopy in the Study of the Reaction of Cellulose with Basic Dyes and Metals

I. N. Ermolenko

Sbornik Dokladov 1-ogo[Pervogo] Nauch. Tekh. Soveshchaniya po Primen. Metodov. Molekulyar. Spektr. Analiza, Minsk (1958) 117–121

Referat. Zhur., Khim., (1959) Abstr. No. 74413

Chem. Abs., **55** (17 Apr 1961) 7846

The reaction of oxidised cellulose with metallic ions and basic dyes was studied by measuring the C:O bands of carboxyl groups during cation sorption. The spectra of oxidised cellulose dyed with Rhodamine 6G (C.I. Basic Red 1), Auramine (C.I. Basic Yellow 2) and Methylene Blue (C.I. Basic Blue 9) showed that all three dyes bring about the same shift of the C:O band toward longer wavelengths and intensity decrease at 1740 cm^{-1} that is seen during sorption of inorganic cations in oxidised cellulose as a result of exchange of the H of the carboxyl groups for metallic ions. This is evidence for an anomalous situation in the absorption mechanism. The characteristic intense bands (in the 7–8 μ region) of these dyes can be used to determine the amount of dye on the fibre, in place of the indirect and laborious methods usually employed. C.O.C.

Physico-chemical Properties of Coacervation Systems useful in Dyeing

B. Milićević and F. Kern

Textil-Rund., **16** (Apr 1961) 190–197

Detailed physico-chemical properties of Cibaphasol C (a fatty acid alkylolamide) solutions are compared with those of oleic acid polyglycol ester and potassium laurate. This compound forms a coacervation system with water in presence of electrolytes, i.e. it separates in two aqueous phases containing different amounts of Cibaphasol. The phase containing the larger proportion of the organic compound is a solvent for many dyes and so can be used to replace an organic carrier in dyeing. The method of using the system in dyeing wool and its advantages over other methods are explained. P.B.S.

Spectroscopic Study of the Mechanism of Dyeing

O. K. Dobozi, L. Lang, and G. Khorvat

Zhur. priklad. khim., **34** (Jan 1961) 204–209

Wool, viscose rayon, nylon, and silk were dyed with a direct dye, Direct Red M (Chemapol) (C.I. 22310), using 1% on the weight of fabric and varying the liquor to goods ratio to obtain the same quantity of dye on each fibre type. Reflection spectra of dyed samples were examined and compared. The effects of dyeing method (neutral or acid) and aftertreatment with metal on the reflection spectra were also examined. Changes in colour corresponding to the displacement of the spectrum of the dye are determined by changes in energy of reaction between the dye and the fibre. Links between the dye and the fibre are heterogeneous in character, some being common to various dye–fibre systems. The actual mechanism of dyeing depends on the structure of fibre and dye, but mainly on the nature, number, and distribution of groups capable of forming secondary valence bonds. L.S.L.

Preparing and Dyeing Trevira–Wool Fabrics

H. Röhser *Melliand Textilber.*, **42** (Mar 1961) 314–317

Trevira (polyester fibre)–wool fabrics require less ironing and are easier to clean than other fabrics, and can be

permanently pleated. Dyeing and finishing are not simple and the following points must be watched. Pilling can be prevented by heat setting, careful shearing, and using yarn of the correct twist. Shrinkage on ironing must not exceed 1% since otherwise trouble will arise in making up or in use. Fabrics must be sufficiently shrunk during preparation, especially in washing and heat setting. The crease recovery after 60 s (both in warp and weft) should be not less than 150°. Heat setting and crabbing are very important in this connection. Carriers employed in dyeing may dissolve small amounts of fatty impurities present in the dye vessel or residues of antistatic agents, lubricants, or spinning oils in the fibres. These may then be deposited on the fabric, producing stains. A water-soluble, easily removable antistatic agent for polyester fibre and a water-soluble spinning preparation for wool have been introduced to facilitate washing. The importance of shrinkage during the different treatments and the factors which affect it are pointed out. Dyeings of different depth require different amounts of carrier, and since concn. of the carrier influences shrinkage and therefore handle it is not possible to obtain the same handle in case of pale and full depths. W.M.

Influence of Liquor Ratio on Exhaustion of Disperse Dyes in High-temperature Dyeing of Polyester Fibres

E. Merian and J. Carbonell

Textil-Rund., **16** (Apr 1961) 181–184

The dependence of exhaustion on dye concentration is investigated for 21 disperse dyes. The effects of liquor ratio and dispersing agent are discussed. It is concluded that the dyeing of polyester fibres conforms to Henry's or Nernst's law. P.B.S.

Dyeing Capron with Metallised Direct Dyes

N. G. Klemin and T. F. Borzova

Tekstil. prom., No. 11 (Nov 1960) 50–52

Capron fabrics have been dyed successfully with metallised direct dyes (Bordeaux Light Fast C, Sky Blue 23, Direct Ruby M) at 100°C (45–60 min) and pH 3-9, yielding intense and bright dyeings. Liquor ratio is 100, dye uptake 75–90%. Good all-round fastness properties and superiority over dyeings of acid dyes are claimed. G.J.K.

Finishing and Dyeing of Agilon D Fabrics

Canadian Textile J., **78** (17 Mar 1961) 43–44

The first finishing treatment of Agilon D fabrics is scouring and bulking to restore the crimp which has been partially removed by tension during winding and knitting. Paddle and rotary drum machines are preferred but winches may be used for ribbed fabrics. The goods are treated in a long detergent liquor with continuous agitation (the temperature being raised from cold to 45°C in 15 min), rinsed and dried with minimum tension. Steam setting, on trays in an autoclave at pressures of 25–27 lb/in², is preferred and the material should be free from creases. The fabric is then bleached or dyed by the conventional methods used for nylon, in a relaxed state with agitation. The various operations in finishing and dyeing are explained in detail. W.P.M.

PATENTS

High-temperature Dyeing of Textiles

A/B Svenska Textilmaskinfabriken

BP 861,035 (Sweden 20 May 1958)

The material is impregnated with dye liquor, wound on a roller and placed into a chamber, which is then closed. The material is then rewound on to a second roller in the chamber and simultaneously heated to fix the dye. It is kept on the second roller at the necessary temperature until the dye is fixed. The material in the closed chamber is heated by steam so that the moisture content of the material is $\geqslant$ 92% of that at 20°C and at "pressure power zero", the latter being obtained by determining the moisture content of the impregnated material under certain pressures, e.g. 1, 2 and 3 kg/cm², and calculating the moisture content under zero pressure by extrapolation. C.O.C.

Improving the Fastness to Rubbing of Azoic Dyeings and Prints

FH *BP* 864,691 (Germany 13 Apr 1957)

The dyeings or prints are treated with a mixture of aliphatic and/or cycloaliphatic and/or aromatic hydrocarbons, one or more surfactants, and aliphatic and/or alicyclic and/or heterocyclic alcohols. Thus an azoic dyeing is, instead of being given the usual aftertreatment, treated for 20 min at 60°C and then for 20 min at 95–100°C in a bath containing water (1000), Na nitrilotriacetate (1), and a mixture (2) of the condensate (20) of 6 mol. ethylene oxide and 1 mol. nonylphenol, tetrachloroethylene (48), butanol (10), oleïn (2), and alcohol (20). C.O.C.

Dyeing Cellulose with Reactive Dyes containing Arylurethane Groups

CFM *BP* 865,681 (Germany 20 Apr 1957)

Water-soluble azo, nitro, or anthraquinone dyes containing at least one NHCO·O·Ar group applied to a cellulose and then fixed by steam or heat in presence of an alkali-metal or NH_4 salt of an organic or inorganic acid or in presence of alkali at a lower temperature yield dyeings which are fast to washing even when the dyes themselves show no affinity for the cellulose. This is because during the process the O·Ar is split off the dye which then chemically combines with the cellulose. Thus cotton cloth is printed with a paste containing the dye 1-aminobenzene-3-sulphonic acid → 2-carbophenoxyamino-5-hydroxy-naphthalene-7-sulphonic acid. After drying, steaming for 5 min at 100–105°C, and soaping, a deep orange print of good fastness to washing and light is obtained. C.O.C.

Dyeing Cellulose Acetate and Triacetate with Acid and Metallised Azo or Azomethine Dyes

BrC *BP* 863,207 (23 Aug 1956)

Acetone-soluble cellulose acetate fibres are treated for 5–120 s at 25–30°C in a bath containing an aqueous solution of the dye, aliphatic alcohol (100–250 g/l.), acetic or formic acid (150–250), and H_2SO_4 (2–8), and then rinsed.

BP 863,208 (23 Aug 1956)

Cellulose triacetate yields full dyeings when dyed by the above process. C.O.C.

Dyes for Polyethylene Terephthalate

FBy *BP* 865,409 (Germany 27 July 1956)

Monoazo dyes of the benzene-azo-benzene, -naphthalene, -pyrazolone, thiazole-azo-benzene or thiadiazole-azo-benzene series, containing no sulphonic or carboxylic groups but containing at least one sulphonylamino group, and in the case of benzene-azo-benzene dyes containing no urethane group, have excellent affinity for polyethylene terephthalate fibres, on which they yield dyeings of good fastness, especially to sublimation. Thus Terylene is dyed orange of good fastness from an aqueous dispersion of 1-amino-2,5-dicyanobenzene → *N*-ethyl-*N*-(methyl-sulphonylamino)ethylaminobenzene. C.O.C.

Vat Dyeing of Polyester Fibres

HH *BP* 863,697 (6 Feb 1959)

Polyester fibres are readily and levelly dyed in an aqueous bath containing a vat dye, thiourea dioxide (C.I. Reducing Agent 11), a protective colloid, a carrier, and a buffer, by gradually bringing the bath to $\leqslant$ 90°C and keeping it at this temperature until dyeing and reoxidation are complete. C.O.C.

Dyeings of Good Fastness to Perspiration on Leather by Use of Azo Dyes containing Phosphonic Acid Groups

FH *BP* 868,142 (Germany 1 Mar 1957)

Dyeings of very good fastness to perspiration are produced on all kinds of chrome-tanned leather by use of azo dyes containing as solubilising groups one or more phosphonic acid radicals. The dyeings are as fast to light as those produced by analogous dyes solubilised by sulphonic acid groups, but have much better wet fastness. C.O.C.

Imparting Red Colour to Cedarwood

Great Western Producers *USP* 2,940,811 (6 Oct 1959)

Wood for pencil slats is treated with a 1–6% aqueous solution of an alkali-metal nitrite so that the wood absorbs 0·03–5·0% of its weight of nitrite. It is then dried for $\leqslant$ 12 h to reduce the water content to $\geqslant$ 10%. The coloured wood so obtained may then if desired be treated in an aqueous dyebath. Alternatively a dye may be added to the nitrite bath. C.O.C.

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m-Dialkylaminophenols as Oxidation Bases for Dyeing Human Hair (IV p. 380)

1,1′-5,1″-Trianthrimide for Mass Coloration of Viscose Rayon (IV p. 385)

Antistatic Finish for Hydrophobic Fibres with Simultaneous Improvement of their Dyeing Properties (X p. 395)

IX— PRINTING

Reactive Dyes in Printing

E. F. Metzger *Teintex*, **26** (15 Apr 1961) 247–254

The historical development of reactive dyes is traced. The basic requirements of reactive dye structures are discussed briefly, leading to a detailed description of the characteristics necessary for reactive dyes in printing, e.g., increased solubility and minimum sensitivity to salt, high stability in moderately conc. alkali at low temperature, sufficient reactivity at increased temperature, formation of a stable chemical link with the fibre, easy removal by washing of non-fixed particles, brightness of hue, and good general fastness. A.T.P.

Effect of the Form of Indanthrone on its Fixation in Printing

S. G. Abramovich

Tekstil. prom., No. 11 (Nov 1960) 45–47

Of the four crystalline forms of Indanthrone (C.I. Vat Blue 4), the one most resistant to over-reduction under printing conditions is the swollen form of the α modification, obtained by treating the γ modification with sulphuric acid. G.J.K.

Printing of PVC

P. P. Birnbaum

Trans. Plastics Inst., **29** (Apr 1961) 60–65

Gravure printing, screen printing, printing by the use of raised surfaces, and planographic methods of printing polyvinyl chloride are considered in some detail, with outlines of the apparatus and the inks and pigments used. W.R.M.

PATENTS

Transfer Positive Films for Textile Printing Rollers

F. Thenhaltor *BP* 862,510 (Austria 27 Feb 1957)

Ink tracings are made for the light, medium, and heavy tones of the original pattern. A negative is then prepared from each tracing, those for the light and medium tones being made by use of a cross-line screen with a ruling angle of 45°, and that for the heavy tones by use of a single-line screen with a ruling angle of 25–30°. The rulings of all the screens have the same pitch. A positive is then prepared from the three negatives and is used in the normal manner to prepare a printing roller. The roller so produced has a common depth of etching for all three tones and so if damaged is easily repaired. C.O.C.

Printed Plastic Floor Coverings

Congoleum–Nairn *USP* 2,943,949 (23 Oct 1957)

Floor covering having a textured three-dimensional printed foamed surface is obtained by printing upon a textured and flexible backing a foamable thermoplastic composition in the form of a multicoloured design and heating to fuse the resin and form the foamed structure. C.O.C.

Photomechanical Colour Reproduction

General Aniline *BP* 865,507 (U.S.A. 17 June 1958)

A process of producing colour separation images by use of negative-working materials so that all the coloured images appear in a single layer. The process enables 4, 5, 6 or more colours to be employed. Appropriate selection of the dyes, coupled with control of the colour density by control of the strength of the dyebath and/or dyeing time, enables extremely accurate matching of the dyed print with that of the corresponding printing ink in a final printed press copy. C.O.C.

Colour or Tonal Correction for Use in Colour Printing

J. F. Crosfield *BP* 866,545 (24 Sept 1958)

A method for colour correcting when making blocks or cylinders for colour printing. C.O.C.

Pressure-sensitive Transfer Sheet

National Cash Register Co.

BP 865,607 (U.S.A. 4 Feb 1959)

A base web is given an undercoating and an overcoating. The overcoat contains a solid marking material and the undercoat a profusion of minute pressure-rupturable capsules each containing a solvent for the marking material. When the coated surface is brought against a receiving surface and local pressure applied, the capsules in the area of pressure are ruptured and the solvent in them released to cause the overcoat there to be dissolved into a paste which is transferred to the receiving surface by the pressure. C.O.C.

Diazotype Printing

R. Landau *BP* 864,011 (France 16 Mar 1957)

Paper or other substrate is coated with a mixture including a diazo compound ("coupler-forming diazo") having weak coupling energy. This compound when irradiated within a predetermined spectral band breaks down into a diazo coupling component. There is also present a diazo compound ("print diazo") which reacts in the dry state with the diazo coupling component to form an azo dye. The diazo compound is also subject to photolysis, which destroys its coupling capacity when it is irradiated within a second predetermined spectral band. Thus paper is coated with a mixture of 1,2-diazoxy-3-dimethylaminomethyl-5-methylbenzene (coupler-forming diazo), 2-diazonium chloride-3-dimethylamino-7-chlorodiphenylene oxide (print diazo), adipic acid, Na adipate and Na 1,6-naphthalene disulphonate. A tracing is placed above the coated paper which is then exposed to visible light or infrared radiation. This destroys all the print diazo except that beneath the lines of tracing. The tracing is then removed and the coated paper subjected to ultraviolet radiation. This breaks down the coupler-forming diazo compound and the resulting coupler immediately couples with the remaining print diazo to yield a positive print. C.O.C.

Photoactivation of Aminotriarylmethane Dye Cyanides

L. Chalkley *USP* 2,936,235 (27 Mar 1957)

Aminotriarylmethane dye cyanides are colourless but become strongly coloured when exposed to ultraviolet radiation in presence of a suitable activator [cf. *USP* 2,676,887. Carboxylic acid amides are much better for this purpose than the previously known activators. Thus paper sensitised with Para Rosaniline cyanide (cf. C.I. 42500) and *N*-methylacetamide yields a red image on exposure to ultraviolet radiation of < 3300 Å and is more sensitive and prints faster than previous Para Rosaniline cyanide sensitised papers.

USP 2,936,276 (25 June 1957)

The salts of *p*-aminotrimethylmethane dye cyanides are photosensitive to different regions of the spectrum than are the free amino compounds. C.O.C.

Multicontrast Photographic Emulsions containing an Oxonol Dye and a Cyanine Dye

Eastman Kodak Co. *USP* 2,944,901 (18 Jan 1957)

Photographic silver halide emulsions showing varying degrees of contrast incorporate a light-absorbing oxonol dye containing a 3-methyl-1-sulphophenyl-5-pyrazolinone nucleus or a barbituric acid (but not thiobarbituric acid) nucleus and as sensitiser either (1) a cyanine dye containing a 5-phenylbenzothiazole nucleus, or (2) a cyanine dye containing $\leqslant 1$ carboxyalkyl group, or (3) a cyanine dye containing $\leqslant 1$ sulphoalkyl group, or (4) a *mero*-cyanine dye containing a carboxyl or sulpho group, or (5) 4-[1,3,3-trimethyl-2(3H)-indolylidene)ethylidene]-3-methyl-1-phenyl-5-pyrazolinone. The sensitising dye must have its maximum absorption in the same region of the spectrum as the oxonol dye and the maximum should be at > 480–500 mμ. C.O.C.

Increasing the Reactivity of Colour Couplers in Photographic Emulsions

Eastman Kodak Co. *USP* 2,945,761 (29 July 1957)

Considerable increase in dye density is obtained upon development, particularly when the colour coupler is in solution in a solvent dispersed in the emulsion, if the developing solution contains n-octylalcohol and a *p*-alkylphenol (Alk of 1–5 C), e.g. *p*-butylphenol. C.O.C.

Copying Subtractive Colour Photographic Films

Ciba *BP* 865,186 (Switzerland 23 Apr 1956)

Monochromatic Direct Positive Coloured Photographic Images

AGFA *BP* 866,203 (Germany 29 Jan 1957)

The above images are produced by treating an exposed silver halide emulsion layer with a colour-forming developer in presence of a coloured coupler which is

converted by the oxidation product of the developer into colourless products. The images are produced in the undeveloped regions of the layer. C.O.C.

Influence of Structural and Mechanical Properties of Printing Inks on their Behaviour during Printing (V p. 388)

Improving the Fastness to Rubbing of Azoic Dyeings and Prints (VIII p. 391)

Floor Coverings from Bitumenised Paper Felt Sealed with Plastics (XIII p. 396)

X—SIZING AND FINISHING

Protection of Textiles Against Attack by Micro-organisms

A. J. Hall *Text. Rec.*, **78** (Apr 1961) 52–55

Various treatments of cotton and rayon, which are readily attacked by fungi and bacteria, are reviewed. Those which depend on chemical impregnation or chemical modification of the material have certain disadvantages when compared with resin treatments. Developments in the resin treatment of fibres are given; and the recommended method is that in which a trimethylolmelamine–formic acid treatment is cured, wet or dry, at elevated temperatures. The conclusion is that resin treatments give a high degree of protection against microbiological attack at reasonable cost. P.B.S.

Embossed Fabric Finishes

R. A. Peel *Dyer*, **125** (7 Apr 1961) 511–514

Description, for apprentices, of the fabric-embossing processes of pre-crêping and after-embossing; and the changes in appearance, handle, and strength of the fabric. There are seven illustrations of rubbings and engraved designs. R.A.P.

Coating Textiles with Polyurethanes

O. Glenz and F. Kassack *Melliand Textilber.*, **42** (Mar 1961) 323–328

Linear polymers of the polyurethane type can be obtained by treating, e.g., hexamethylene diisocyanate with butylene glycol, but such compounds are not suitable for coatings. Cross-linked polymers can be produced by using as alcoholic component a polyester (e.g. the condensation product of adipic acid and glycol) and adding small amounts of a tri-functional substance (glycerol). Such strongly cross-linked polymers are, however, too hard and brittle for coating. A new product, Impramil, based on polyester and isocyanate and which contains comparatively few but regularly spaced cross-linkages, has been introduced. It is said to give satisfactory softness, handle, and permanence. Recipes for clear and coloured coatings are given and machines for application are described. The coatings obtained are claimed to be very soft and to retain flexibility down to −40°C, and are especially recommended where mechanically resistant coatings without great increase in weight are required. W.M.

Role of Spiral Structure in Untreated and Treated Cottons

R. S. Orr, A. W. Burgis, L. B. DeLuca, and J. N. Grant *Text. Research J.*, **31** (Apr 1961) 302–310

Study of the untwisting of the spiral structure as a load was applied to the fibre shows that reversals are a vital structural feature which affects the twisting. A reversing spirality represents an idealised structure for obtaining optimum strength, elongation, and elastic recovery from the straight-chain molecules of cellulose. Friction between growth layers and fibrils in such a structure is a possible cause of permanent set, low intrinsic strength of highly orientated cotton, and the weak points near the reversals. The spiral structure persists through mercerisation even under tension; however, the X-ray angle is appreciably reduced. The high alignment achieved by resin treatment of cotton under tension causes reduction in elongation and increase in strength compared with treatment in absence of tension. The high alignment in cotton resin-treated under tension persists through washing in an aqueous solution of a detergent. Differences between properties of cotton are reduced but not eliminated by mercerising and resin-treatment, but important remaining differences indicate the importance of selecting cottons of optimum quality for various end-uses. C.O.C.

Cross-linking of Cotton Cellulose. II—Microscopical Observations

V. W. Tripp, A. T. Moore, and M. L. Rollins *Text. Research J.*, **31** (Apr 1961) 295–302

Significant increase in primary lateral bonding between cellulose chains introduced under dry conditions reduces the swelling ability of the fibre and the ease with which fibrillation is achieved by wet beating. There is much less cleavage of the fibre along natural lines, i.e. between lamellae of the cell wall. Separation of lamellae by either wet beating or controlled swelling is greatly reduced. Concomitant with these changes is increase in brittleness of the cellulose structure, leading to formation of short, jagged fragments under the same conditions of mechanical stress which give long, stringy formations in non-cross-linked fibres. Cross-linking of swollen cellulose yields a product differing from the foregoing in that wet beating generally results in cleavage of the cellulose along the lines of the lamellae. The situation and distribution of cross-links in the two sets of fibres are undoubtedly different. A water-swollen fibre is about 30% larger in cross-section than a dry fibre; in presence of 20% NaOH its cross-section is about double that of a dry fibre. Thus the distance between adjacent cellulose chains is much greater under these conditions. If the surface of the microfibrils and regions along their length are not as highly ordered or as compact under swollen conditions, the concentration of new lateral bonds in such areas will be lower. Joining of microfibrils from adjacent layers will be less frequent, resulting in inability of the structure to exclude water. Such a high distribution of cross-links will not produce high dry crease recovery, as the bonding involved in the recovery does not come into play until a swollen state is reached. It is improbable that the highly ordered regions of the fibre would undergo cross-linking when dry, so that lateral bonding would in such cases be present to the greatest extent in the regions of low lateral order. The microfibrillate structure proposed by Frey-Wyssling (*Science*, **119** (1954) 80–82), involving a paracrystalline mantle on the microfibrils, seems to be a useful concept in this respect. It accounts for the possibility of cross-linking between chains near the surface of the same microfibril and between chains of adjacent microfibrils. Assuming 20% of the anhydroglucose units are accessible, then a cross-link would be present between every second pair of these units at a degree of substitution of 0·05. Several typical cross-linking agents appear to give maximum effect in recovery properties at this level of reaction. Under these conditions much of the cellulose would be insoluble, and this has been observed. However, if cross-linking is done in the swollen state, the cross-links will be less concentrated and a much larger number would be required to impart comparable elastic recovery. C.O.C.

Chemical Modification of Cotton with Derivatives of Divinyl Sulphone

G. C. Tesoro, P. Linden, and S. B. Sello *Text. Research J.*, **31** (Apr 1961) 283–295

Addition of divinyl sulphone to cotton to form cross-linked cellulose ethers can impart excellent wash-and-wear properties, but the great danger and difficulties associated with the handling of divinyl sulphone discourage extensive use of this reagent even in the laboratory. Converting divinyl sulphone into non-volatile and relatively non-toxic water-soluble derivatives which can be padded into fabrics, enables addition of the sulphone to cellulose to be carried out under controlled conditions with complete avoidance of the dangerous aspects of the divinyl sulphone reaction. In addition, use of the derivatives allows greater flexibility in method of application, minimises side reactions and yields better products with greater efficiency. Cotton cloths treated with these derivatives have greatly improved wet crease recovery, moderately improved dry crease recovery, and some loss of tensile and tear strength. Use of softeners increases tear strength, abrasion resistance, and dry crease recovery of sulphone-treated cloths. The wash-and-wear performance of the treated cloths is excellent, being significantly higher than might be predicted on the basis of crease-recovery measurements alone. C.O.C.

Response of Cottons to Chemical Treatments. III—Resin Finishing of Yarn
L. Rebenfeld *Text. Research J.*, 31 (Apr 1961) 311–316
Tests on resin-finished yarns made from six widely different cottons indicate that the cottons respond differently to chemical treatments, e.g. resin finishing. Many changes in fibre properties caused by the treatment can be related to fibre structure. The work confirms that the cotton fibre is an important variable in chemical finishing treatments. C.O.C.

Self-smoothing Cotton
J. T. Marsh *Text. Manuf.*, 87 (Apr 1961) 153–156
The use of dimethylolethylurea in resin treatment of cotton to impart wash-and-wear properties is examined. Home laundering, in general, does not lead to chlorine retention or loss of fabric strength, but commercial laundering can give widely differing results, depending on the processing cycle. In theory, dimethylolethyleneurea should not provide sites for chlorine retention after hypochlorite bleaching, but in practice such sites exist to a small extent; the influence of such factors as catalyst efficiency and sensitivity to acid conditions, storage, and steaming is discussed, and possible explanations of the development of chlorine retention are suggested. S.B.D.

Resin-containing and Resin-free Finishes with Special Reference to the Wash-and-Wear Finish
G. Pusch *Melliand Textilber.*, 42 (Mar 1961) 328–334
Finishes based on cyclic urea "reactant" resins have excellent fastness to washing at the boil and a very good wash-and-wear effect but the resistance to chlorine is poor. Triazine resins are much better in this respect but yellow on ironing (not because of chlorine retention). Resins free from nitrogen (epoxy and acetal compounds) produce a very good wash-and-wear effect but only moderate crease recovery, and do not retain chlorine. The handle of the treated material is very soft. Resin-free finishes based on dichlorohydrin and epichlorohydrin were tested. Both compounds produce cross-linking. The wet crease recovery is good, but the dry crease recovery poor, and there is hardly any wash-and-wear effect. W.M.

Survey of Antishrink Finishes for Wool
Tex, 20 (Apr 1961) 164–169
The two main principles involved, chemical action and resin-treatment, are described, and the following commercial processes discussed briefly: Aktivin, Melafix, Negafel, Harrisat, Dylan, WIRA, Maxifix, Lanfix, Tootal, Perzyme, Chlorzyme, CSIRO, Lanaset. R.A.

Competition as Driving Force in Synthetic-fibre Finishing
J. G. Evans *Chemiefasern*, 11 (Apr 1961) 258–261
The main topic of this review is the creasing properties of fabrics. Finished viscose rayon fabrics should have good form stability, satisfactory handle, and good wet and dry crease recovery. The requisite finishing properties for various washing and drying techniques are compared. Attention is drawn to the current search for methods of improving wet crease recovery, e.g. by cross-linking. Cross-linking methods are shown to be superior to resin treatments— cross-linking of cellulose in the swollen rather than anhydrous condition giving the best retention of physical properties. Some details of known processes for cross-linking, applicable mainly to cotton, are given, i.e. Belfast Process (Deering Milliken Co. U.S.A.), Wonder Dry-Finish (Calico Printers Assocn.) and Prystene Finish (Bradford Dyers Assocn.). I.G.L.

Fastness of Dyed Textiles to Pleating Processes
H. R. Hadfield
Canadian Textile J., 78 (17 Mar 1961) 52–62
Hydrophobic synthetic-polymer fibres and new resin finishes for cellulosic fibres have resulted in a demand for dyed materials possessing high colour fastness to pleating and setting processes. In the case of natural-fibre fabrics, steaming treatments are generally employed to produce pleated effects. Dry-heat treatments also are common for synthetic-polymer fibres. Steam pleating and setting processes and dry-heat pleating and setting processes are outlined and the ways in which the variables affect the fastness of dyed textiles are discussed in relation to the development of reliable laboratory fastness tests. The various standard tests which have been advocated for assessment of steam and dry-heat fastness are compared, and the development of the S.D.C. standard tests, including the design of apparatus, is described and discussed. W.P.M.

PATENTS

Resin Finish
Chemische Fabrik Duren
BP 864,432 (Germany 9 Apr 1957)
Cellulosic fabrics are treated with a condensate of HCHO and a compound of formula $H–(UZ)_nU–H$ (n = 1–4; U = urea, thiourea, guanidine, dicyandiamidine, or mono- or di-(*N*-Alk or *N*-Ar) derivatives thereof and from which 2, 3 or 4 H atoms have been removed; Z = either a cyclic group or an aliphatic chain which may be substituted by basic or neutral groups), e.g. the compound obtained from urea (3 mol.) and a diamine (2 mol.). This imparts good crease recovery without loss of tensile strength or resistance to abrasion. The finished goods have no tendency to retain chlorine when treated with hypochlorite. C.O.C.

Protecting Fibrous Cellulosic Material from Attack by Micro-organisms
Ciba *BP* 863,514 (Switzerland 9 Sept 1958)
Cellulosic material, particularly that having a low swelling value, is impregnated with an aqueous composition containing a hardenable aminoplast and a catalyst and then, without drying, the aminoplast is cured. C.O.C.

Resin Treatment of Textiles
Shri Ram Institute for Industrial Research
BP 861,693 (India 4 Mar 1957)
Resin deposited on the surface of the materials during padding can be removed by passing them through a fluidised bed of a hydrophilic material. Thus cotton cloth was impregnated with 80% of its weight of an aqueous solution of a urea–formaldehyde precondensate and then dried by passing for 20 s through a fluidised bed of 100–150 mesh bentonite at 120°C. It was then brushed free of bentonite and cured by passing for 20 s through a fluidised bed of 40–60 mesh sand at 165°C. The finished fabric had a firm soft handle and showed no loss in tensile strength. C.O.C.

Press-free Pleat-retaining Garments
Koret of California *BP* 862,653 (20 May 1957)
Garments which retain their pleats despite numerous washings after which they need neither ironing nor pressing are obtained by making the garments from fabric that has been impregnated with 70–80% of its weight of an aqueous solution of a thermosetting resin and dried below curing temperature. Curing by baking is done only after the garment has been made and the necessary pleats have been inserted. C.O.C.

Water-repellent Finish
Chemische Fabrik Pfersee
BP 862,197 (Germany 20 Feb 1958)
A water-repellent finish of outstanding fastness to washing and dry-cleaning is obtained by treatment with a silicone and a product obtained by condensing aminoplast-forming *N*-compounds, formaldehyde, aliphatic monocarboxylic acids of > 10 C, and/or resinic acids with an alkanolamine in presence of a hardening agent for the silicone. C.O.C.

Grafting of Cellulose Acetate
Société des Usines Chimiques Rhône-Poulenc
BP 865,263 (France 26 Feb 1959)
Cellulose acetate fibres, film, etc. are impregnated with an addition-polymerisation catalyst and then treated with the hot mixed vapours of an addition-polymerisable monomer and a non-reactive liquid. Thus cellulose acetate fibre is immersed for 1 min in a 1·7% solution of benzoyl peroxide in methanol. It is then passed for 2 min through the vapour coming from an equi-volume mixture of vinyl acetate and heptane. This yields fibres of much increased resistance to degradation by ultraviolet radiation. C.O.C.

Antistatic Finish for Hydrophobic Fibres with Simultaneous Improvement of their Dyeing Properties
Onyx Oil & Chemical Co.
BP 864,791 (U.S.A. 17 June 1957)

Compounds of formula

$$XCH_2CH_2(OCH_2CH_2)_mORO(CH_2CH_2O)_nCH_2CH_2X$$

(X = ester-forming residue of an inorganic acid or of an organically substituted sulphuric, phosphoric, or sulphonic acid; m and n = 3–40; R = glycol), e.g. polyethyleneglycol di-*p*-toluene sulphonate, are applied to the fibres and then baked. Thus the product obtained by heating under pressure methylamine, polyethyleneglycol dichloride, ethylene glycol, and soda ash, applied from aqueous solution to nylon or polyester fabric, dried and baked for 3 min at 150°C, yields an antistatic finish fast to repeated washing. The process also imparts to hydrophobic fibres good affinity for acid dyes. C.O.C.

Rendering Polyamide Fibres more Water-absorbent
FBy *BP* 861,875 (Germany 28 Sept 1957)

Modification of *BP* 757,274 (*J.S.D.C.*, **72** (1956) 615), the same effect being obtained by using a uniform polyamide, e.g. a polyamide of aminocaproic acid, instead of a mixed polyamide. This offers the advantage that an aqueous organic acid emulsion may be used as well as an aqueous alcoholic emulsion. C.O.C.

Coated Polyamide or Polyester Fibres which do not Drip when Exposed to Flame
FH *BP* 863,738 (Germany 4 June 1957)

The fabric is coated with a plastisol containing Sb_2O_3. Thus a nylon fabric was thinly coated with a plasticised polyvinyl chloride paste containing no pigment but containing a substance imparting adhesive properties, e.g. toluene di-isocyanate. It was then given three coatings of a composition made up of polyvinyl chloride, dioctylphthalate, Sb_2O_3, lithopone, and dye. After each of these four coatings the material was pregelled at 120°C. After one side of the fabric was coated, the other was coated in the same manner and the whole gelled for 5 min at 170°C. The coated fabric did not drip under the prolonged action of a gas flame and did not continue to burn after removal of the flame. C.O.C.

Improving the Adhesion of Fibrous Materials to Rubber
Esso Research & Engineering Co.
BP 861,814 (U.S.A. 3 May 1957)

The material is first coated with a phenolic-aldehyde resin-containing rubber latex (not a butadiene–styrene–vinyl pyridine latex) and then with a brominated butyl rubber. Such coated material has good adhesion to rubber subsequently applied to it. C.O.C.

Reflex-reflecting Textile Yarns and Fabrics
Minnesota Mining and Manufacturing Co.
BP 862,141 (U.S.A. 29 Oct 1956)

The yarn has a durable and flexible coating in which is embedded a concentric surface layer of half-embedded catadioptric reflex-reflecting elements consisting of minute glass beads made specularly reflective by being plated with metal on their embedded surface. Thus the yarn is coated with a vulcanisable rubbery binder and then a surface layer of metal-plated, glass microspheres of refractive index 1·9 is applied. The yarn is then dried, cured and passed through a liquid which removes the metal from the exposed surface of the microspheres. C.O.C.

Bonded-fibre Fabric
C. Harmon *BP* 864,246 (U.S.A. 26 Mar 1958)

The binding agent is applied in a pattern. The fabric is then selectively crimped or crinkled so that the portions containing the binder remain smooth while the remaining portions are crimped and crinkled. This yields a fabric having good elasticity, pliability, a soft handle and a characteristic appearance. C.O.C.

Theory of Drying of Drying Oils (V p. 387)
Preparing and Dyeing Trevira–Wool Fabrics (VIII p. 390)
Finishing and Dyeing of Agilon D Fabrics (VIII p. 391)
Printed Plastic Floor Coverings (IX p. 392)
Coating Porous Materials (XI p. 396)
Coating with Hydrocarbon Resins (XIII p. 397)
Curing Organopolysiloxanes (XIII p. 397)

XI— PAPER AND OTHER CELLULOSIC PRODUCTS

Relationship between Alkali Solubility and Percentage of Short Chains in Native and Regenerated Celluloses
A. Keil, B. Philipp, and R. Jacob
Faserforsch. und Textiltech., **12** (Mar 1961) 94–105

The increase in alkali solubility of cellulose samples resulting from addition of zinc oxide to the caustic soda solution or lowering of the extraction temperature is studied. The effect of various pretreatments of the cellulose is examined and the variation in D.P. of the extracted material with extraction method and nature of cellulose is studied. A short-chain fractionation method involving extraction with aqueous solutions containing zinc oxide and caustic soda, and the viscometric determination of the D.P. of the extracted material, are described. W.R.M.

Readily Hydrolysable Fraction of Wood Cellulose
I. I. Korol'kov and G. D. Paramonova
Zhur. priklad. khim., **33** (Dec 1960) 2739–2743

Kinetic data of the hydrolysis and ethanolysis of wood pulp permit a semiquantitative assessment of the readily hydrolysable fraction of cellulose. G.J.K.

Hydrolysis of Polysaccharides of Plant Tissue by Concentrated Hydrochloric Acid and Gaseous Hydrogen Chloride
N. V. Chalov, A. E. Leshchuk, and O. A. Aleksandrova
Zhur. priklad. khim., **33** (Dec 1960) 2743–2750

The undesirable effects of high temp. on the hydrolysis of polysaccharides are avoided by soaking the plant tissue with cold conc. HCl (> 41%) and subsequently saturating the mixture with HCl gas at atmospheric pressure. This enables the hydrolysis to be carried out at the optimum temp. of 20–25°C. Application of the procedure to wood pulp enables the hydrolysis to be carried out six times more rapidly and with a specific uptake of HCl 1·5 times less than when hydrolysing with 41% HCl in a diffusion battery. G.J.K.

Bonding of Cellulose to Lignin in Plant Tissue
B. I. Stepanov, A. I. Skrigan, A. M. Shishko, and R. G. Zhbankov *Doklady Akad. Nauk. S.S.S.R.*, **135**, No. 3 (21 Nov 1960) 624–626

Bonding of cellulose to lignin is investigated by submitting woody materials of different ages to alkaline scour in 12% NaOD (I) and 12% NaOH (II), respectively, and by comparing the IR spectra of the celluloses thus obtained with the spectrum of pure cotton cellulose (III) treated identically with 12% NaOD. II and III show close similarity in the region 1300–1400 cm^{-1} but differ from I, and this is attributed to chemical bonding to lignin at the C_6 atom. However, the presence of a very intense OH band in I indicates that most of the OH groups in cellulose are apparently not involved in bonding to lignin. G.J.K.

PATENTS

Size for Paper
British Bewoid Co. *BP* 867,924 (31 Mar 1958)

Soap or rosin dispersion sizes are given much better sizing efficiency by adding to them a rosin ester formed with a compound containing a >C:C–CO·O– group, e.g. rosin treated with an $\alpha\beta$-unsatd. acid and then esterified. C.O.C.

Coating Paper on Both Sides
Champion Paper & Fibre Co.
USP 2,946,307 (23 Dec 1955)

Excess of coating composition is applied to one surface and the surplus removed by a small-diameter, rotating doctor rod carried by a spring mounting which presses it against the freshly coated surface of the paper while the paper is backed up by a rubber-covered roll. The paper passes around the doctor rod so that the non-coated side of the paper only touches the rubber-covered roll momentarily as it passes between the doctor rod and the roll. Coating composition is applied to the rubber-covered roll and transferred to the paper during its passage between the doctor rod and the roll. The roll need not necessarily rotate at the speed of the paper. Difference in speed of the two gives a wiping action in connection with the transfer and this wiping action is often

advantageous and results in a coating on the paper which is thicker or thinner than that applied to the rubber-surfaced roll before transfer of the composition to the paper. C.O.C.

Pigmented Paper
Columbia-Southern Chemical Corpn.
USP 2,943,971 (31 July 1959)

Good retention of the pigments and substantial reduction in costs without sacrificing the quality of the paper is obtained by using a pulp slurry containing both TiO_2 (C.I. Pigment White 6) and an amorphous siliceous pigment, preferably Ca silicate. By this means up to 90% of the TiO_2 normally required may be replaced by the much cheaper Ca silicate. C.O.C.

Coating Paper with a Styrene Polymer
Monsanto Chemical Co. *BP* 867,779 (U.S.A. 7 Nov 1956)

Paper is coated with an aqueous dispersion of (*a*) a thermoplastic styrene polymer (100 parts by wt.) and (*b*) an organic solvent for the polymer (10–75) of b.p. 175–325°F. The coating is finally set by heating to 50 deg F above the b.p. of the solvent. This gives the paper a smooth impermeable coating. The dispersion used may contain colorants. C.O.C.

Drying Paper Webs
E. A. Timson *BP* 868,679 (19 Feb 1958)

One or more naked flames play between opposed surfaces or spaced straight runs of two travelling webs. The method is particularly suitable for printing machines where two webs are run on adjacent courses, both of which need drying. R.A.

Web Drying
Dominion Engineering Works
BP 868,843 (15 July 1957)

Streams of hot air are made to flow over both sides of a travelling web of paper or similar product, in a direction opposite to the direction of travel of the web. R.A.

Coating Porous Materials
Riegel Paper Corpn. *BP* 864,309 (U.S.A. 18 Feb 1957)

A layer of a non-porous material is sandwiched between two layers of web at least one of which is porous. The intermediate layer is heat-softenable at a temperature which does not adversely affect the porous material. The assembly is then bonded together with a bond strength in excess of the cohesive strength of the intermediate layer when it is softened by heat. The two outer layers are then separated while the intermediate layer is hot so as to split it along a centre plane between the two outer layers. This renders the intermediate layer porous through to the two outer layers which are now coated with it. C.O.C.

Drying Rollers for Paper Felts (I p. 374)
Grafting of Cellulose Acetate (X p. 394)
Removal of Organic Coatings (XIII this page)
Butadiene–Styrene Copolymer Latices for Coated Printing Papers and Boards (XIII this page)
Floor Coverings from Bitumenised Paper Felt Sealed with Plastics (XIII this page)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Studies in Fellmongering. II—Influence of Curing and Soaking Conditions and of Temperature of Sweating (VI p. 389)
Electron Microscopic Structure of Collagen (VI p. 389)
Rapid Moisture Determination in Leather (XIV p. 399)

XIII—RUBBER; RESINS; PLASTICS

Reactive Diluents for Epoxy Adhesives
C. A. May and A. C. Nixon
Ind. Eng. Chem., **53** (Apr 1961) 303–304

The inclusion of plasticisers or solvents in the formulation of paste adhesives leads to greatly reduced bond strength. To overcome this defect, diluents containing epoxy groups which become chemically bound in the system can be used. The results of a study of seven such diluents is expressed in terms of bond strengths at room temperature and at 300°F. P.B.S.

Removal of Organic Coatings
L. R. Brantley *Ind. Eng. Chem.*, **53** (Apr 1961) 310

The Adherometer is used to measure the force necessary to strip an organic coating from metal panels. A new unit is proposed, the "mil-hesion", which is the interpolated value of the stripping force for a coating of 1-mil thickness. The use of the above instrument in the testing of alkyd, nitrocellulose, and pigmented ethyl cellulose coatings is reported briefly. P.B.S.

Butadiene–Styrene Copolymer Latices for Coated Printing Papers and Boards
Plastics, **26** (Mar 1961) 113–116

Correlation and discussion of data obtained by ICI Plastics Division, relating to the use of a butadiene–methyl methacrylate (*sic*) copolymer latex as partial replacement for casein or starch in compositions for the coating of papers and boards for printing. Modification of composition is discussed in relation to the following—coating solids, pick resistance, wet-rub resistance, calendered gloss, varnish gloss, wax hold-out, coating flexibility, ink receptivity, and printability. J.W.D.

Mechanism Underlying the Wear of Polymers by Rubbing
S. B. Ratner *Dokladÿ Akad. Nauk S.S.S.R.*, **135**, No. 2 (11 Nov 1960) 294–297

The mechanism underlying the wear of a wide range of polymers by rubbing is investigated. In elastic polymers (e.g. ebonite), rubbing with a metal gauze produces transverse bands on the surface (friction pattern) whilst rubbing with fur yields longitudinal bands (abrasion pattern). On the other hand, the more plastic type of polymers (e.g. fluoroplasts) yield longitudinal bands with both metal gauze and fur. G.J.K.

Influence of the Carbon Black Surface on its Reaction with Sulphur and Rubber and on the Kinetics of Vulcanisation
V. A. Dogadkin, Z. V. Skorodumova, and M. S. Fel'dshtein
Kolloid. zhur., **22** (Nov–Dec 1960) 663–670

The presence on the surface of Carbon Black pigment of oxygen-containing groups adversely affects its ability to absorb rubber latex. This is true for solutions of rubber in n-heptane and mixtures of rubber prepared by mastication and subjected to vulcanising temperatures. Sulphur is chemically adsorbed on the carbon surface and participates in cross-linking during vulcanisation. Oxidation of Carbon Black surface causes an increase in acidity which in turn retards the vulcanisation process, decreases the amount of chemically combined sulphur, and decreases the modulus. L.S.L.

Plastics in Theory and Practice
G. Gee *Trans. Plastics Inst.*, **29** (Apr 1961) 32–38

(First Swinburne Award Address.) Some aspects of polymerisation are outlined, polymer processing problems are considered in terms of fluid flow, and bulk properties of polymers in relation to chemical structure and chain flexibility. W.R.M.

Frictional Properties of Thermoplastics
Plastics, **26** (Mar 1961) 117–118

Collation, with ten references, of work (both published and unpublished) on the frictional properties of thermoplastic materials, with particular reference to polythene, nylon, and polytetrafluoroethylene. Results vary with the method of test used, temp., and moisture content (particularly with nylon), and the coefficient of friction of a given material may vary according as the plastics material is the static or the sliding member during test. J.W.D.

Review of Plastics for 1960
Modern Plastics, **38** (5) (1961) 141 *et seq.*
Chem. Abs., **55** (17 Apr 1961) 7890

590 References. C.O.C.

PATENTS

Floor Coverings from Bitumenised Paper Felt Sealed with Plastics
BASF *BP* 869,434 (Germany 26 Sept 1958)

Bitumenised paper felt is sealed with an aqueous dispersion of a copolymer of vinylidene chloride (20–90% by wt.), an acrylic ester and/or carboxylic vinyl ester (> 80) and vinyl chloride (> 40). This gives a sealing layer

which is very flexible and resistant to water and bitumen and which serves as an excellent support for the subsequent printing and lacquering. C.O.C.

Coating with Hydrocarbon Resins
DuP *BP* 863,769 (U.S.A. 14 Apr 1958)

A composition comprising a polymer of a mono-olefinic hydrocarbon of melt index 0·1–10·0 and 0·25–10·0% by weight of a polyallyl ester of cyanuric acid of a polyallyl melamine is applied, e.g. to aluminium foil, at 170–300°C under pressure. It can also be used as an adhesive, e.g. to bond aluminium foil to polyester film. C.O.C.

Curing Organopolysiloxanes
Midland Silicones *BP* 862,844 (U.S.A. 9 Aug 1957)

An organosiloxane, all of whose organic radicals are aliphatic or cycloaliphatic hydrocarbon radicals which may be halogenated, is cured by exposing it to ozone either at < 80°C but at a temperature sufficiently high to effect curing or at < 80°C and below curing temperature, and then bringing it, in absence of ozone, to curing temperature. C.O.C.

Cross-linking of Polyvinyl Alcohol
Th. Goldschmidt *BP* 870,438 (Germany 31 Jan 1959)

Treatment with cyanuric chloride in alkaline medium cross-links polyvinyl alcohol and so reduces its solubility and/or swellability in water. C.O.C.

Protecting Halogen-containing Polyester Resins against Outdoor Exposure
Hooker Chemical Corpn. *BP* 865,408 (U.S.A. 27 Aug 1956)

Coating with a solid synthetic resin together with $\leq 1\%$ by wt. of the resin of a 2-hydroxybenzophenone gives polymerised halogen-containing polyesters excellent protection against outdoor exposure. C.O.C.

Linear Polyester Films Suitable for Writing Upon
Kalle *BP* 870,330 (Germany 3 Mar 1959)

Polyester film is given a matt surface which can be written upon by coating it with a mixture of polymeric terephthalic mixed esters of an inert powder, e.g. glass powder, of particle size $< 30\ \mu$. C.O.C.

Coating Polystyrene
Plax Corpn. *BP* 870,437 (U.S.A. 23 Dec 1958)

An aqueous emulsion containing 15–40% by wt. of a thermoplastic copolymer and 0·2–4·0% by wt. of a water-soluble thermosetting aldehyde–amine precondensate, applied to polystyrene and then dried and cured yields a firmly adherent, transparent, non-crazing coating. C.O.C.

Solvent for Vinyl Chloride–Vinyl Acetate Copolymers (III p. 377)
Structure of Dispersed Carbon Blacks (C.I. Pigment Black 6 and 7) (V p. 388)
Printed Plastic Floor Coverings (IX p. 392)
Coating Textiles with Polyurethanes (X p. 393)
Natural and Synthetic Rubbers (XIV p. 399)

XIV—ANALYSIS; TESTING; APPARATUS

Use of Activation Analysis in Textile Chemistry
F. Münzel and H. Krässig
Textil-Rund., **16** (Apr 1961) 204–207

The method depends on the fact that a large number of elements are converted by irradiation with slow thermal neutrons to radioactive isotopes. Material is irradiated in a reactor or with an antimony–beryllium source. Then radiation from the isotopes is measured with a gamma-ray spectrometer, a beta-ray absorptiometer, or by the film contact method. An example is given in which residual chlorine is determined in a fabric, a procedure which would not be possible by conventional methods. P.B.S.

Increasing Selectivity of Analytical Reactions by Masking
K. L. Cheng *Anal. Chem.*, **33** (May 1961) 783–790

A review of masking and demasking reactions and their theoretical treatment. P.B.S.

Determination of the Density of Crystals
D. M. Cooke and J. O. Warwicker
Chem. and Ind., No. 16 (22 Apr 1961) 504–505

Describes the calibration and use of density-gradient columns to show the range of density of a batch of crystals, from which a correct density can be derived. The highest density for any given batch was found to be nearest to that calculated from X-ray data. P.B.S.

Apparatus for Shaking a Large Number of Flasks
P. E. Ballance
Chem. and Ind., No. 16 (22 Apr 1961) 503–504

This consists of a frame carrying two pairs of flask-carrying trays, such that the pairs of trays move in opposite directions (one above the other). Oscillatory motion is provided by an electric motor. Advantages claimed are: that it is inexpensively and rapidly built or dismantled; a large number of flasks can be carried (144×350 ml); the moving parts are almost completely silent. P.B.S.

Simple Method of Identifying Emulsion Types and Testing Their Stability
H. Tronnier and H. Bussius
Seifen-Öle-Fette-Wachse, **86** (1960) 747–748
Chem. Abs., **55** (3 Apr 1961) 6890

Filter paper discs are soaked in 20% aq. $CoCl_2$, dried at 60–80°C and kept in a desiccator. A drop of the emulsion is placed on the dry, blue paper disc. Oil-in-water emulsions immediately turn the paper pink throughout and a pink halo forms on the surface of the paper around the drop. Water-in-oil emulsions cause only a fatty halo with no colour change. Mixed-type emulsions cause, after about 20 min, the surface only of the paper in contact with the emulsion to become a weak pink. C.O.C.

Water Analysis
W. Skougstad and M. J. Fishman
Anal. Chem., **33** (Apr 1961) 139R–164R

A review of analytical methods for the two-year period ending August 1960. P.B.S.

Thorin—Chromogenic Agent and Chelatochrome Indicator
M. B. Johnston, A. J. Barnard, and W. C. Broad
Rev. unit. ind. Santander, **2** (1960) 137–146
Chem. Abs., **58** (17 Apr 1961) 7144

Review, 102 references. C.O.C.

Salarcid—A New Reagent for the Complexometric Determination of Iron
L. S. Malowan and M. Alegre
Ciencia (Mex.), **20** (1960) 205–206
Chem. Abs., **55** (17 Apr 1961) 7144

Salicylaldehyde semicarbazide (salarcid) is a sensitive reagent for Fe^{3+}, in presence of which it turns blackish green. It permits determination of Fe by using di-Na EDTA. The results agree well with theory. C.O.C.

New Class of Indicators for Determining pH in Coloured Aqueous Solutions
A. Kotiǫnis *Chim. Chronica, Spec. ed.*, (1957) 25–28
Chem. Abs., **55** (17 Apr 1961) 7144

Describes a method based on adding to the solution to be tested an organic non-polar solvent and a suitable organic base, the partition coefficient of which between the two phases is a function of pH. Quinone and Bromophenol Blue with $CHCl_3$ is a good indicator for pH 3·4–5·2. C.O.C.

Applications of Complementary Tristimulus Colorimetry
H. Flaschka

I—Analysis of Binary and Ternary Colorant Systems
Talanta, **7** (1960) 90–106

Complementary tristimulus colorimetry can be applied to the analysis of binary and ternary mixtures of colorants. Relation to the human eye is unnecessary, only the designations of the various parameters and the mode of calculation need be retained. The binary system of the EDTA complexes of Cu and Ni and ternary system of the EDTA complexes of Cu, Ni, and Co are treated in detail to illustrate the new approach. Results can be calculated graphically or purely algebraically, or in a combined graphical and algebraical manner the relation of the new approach to classical photometric analysis of multi-component systems can be shown.

II—A Least Square Method Applied to Multi-component Systems

Ibid., **8** (1961) 8–15
Chem. Abs., **55** (17 Apr 1961) 7138

Calculation of colorant concentrations in tristimulus colorimetry can be improved by application of the least square method, rather than by simple averaging of sets of results. In this improvement a matrix approach is especially useful, and the required equations are developed. Comparison of results obtained by both methods shows the superiority of the matrix approach. C.O.C.

Colorimetric Detection and Determination of Aromatic Amines with 3-Methyl-2-benzothiazolone Hydrazone

E. Sawicki, T. W. Stanley, T. R. Hauser, W. Elbert, and J. L. Noe *Anal. Chem.*, **33** (May 1961) 722–725

This new reagent forms azo compounds with many amines in presence of ferric chloride. A table showing colour, wavelength maxima, molar absorbance, and limits of identification for approx. 100 amines is given. Aliphatic aldehydes, ketones, and phenols interfere with the colour reaction and an extraction method is proposed to overcome this trouble. P.B.S.

Paper Chromatography of Sudan Dyes

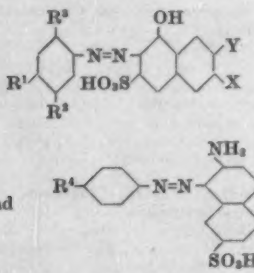
J. Chromatography, **5** (Apr 1961) D17

R_f values, collected from J. Gasparič and M. Matrka, *Collection Czechoslov. Chem. Communs.*, **25** (1960) 1969, are given for the following Sudan dyes— C.I. Solvent Yellow 1, 2, 14, 18 and 29, C.I. Solvent Orange 7 and 8, C.I. Solvent Red 1, 18, 23, 24 and 25, C.I. Solvent Brown 1, 2 and 5, and C.I. Solvent Black 3. Whatman No. 3 paper, impregnated with 50% dimethylformamide in ethanol, 10% liquid paraffin in hexane, and 50% lauryl alcohol in ethanol, was used. Elution was by means of cyclohexane, ethanol–water (4:1) and (1:1), ethanol–ammonia (4:1) and (1:1). F.J.

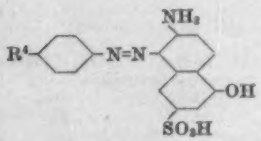
Chromatography and Electrophoretic Mobilities of Some Azo Dyes

J. Chromatography, **5** (Apr 1961) D18–D19

R_f values of eleven azo dyes based on the structures



and



where R^1 = H, SO_3H or NO_2; R^2 = H or SO_3H; R^3 = H or OH; X and Y = H or NH_2; and R^4 = H, NO_2 or SO_3H; have been found by J. Franc and M. Wurst, *Collection Czechoslov. Chem. Communs.*, **25** (1960) 663. Whatman No. 1 paper impregnated with 30% liquid paraffin in cyclohexane was used and solvents were 80% aq. ethanol and ethanol–3-N ammonia (4:1). Electrophoretic mobilities of the above dyes, using 3-N ammonia and N acetic acid, are given. F.J.

Intermediates in Food, Drug and Cosmetic Colours

W. B. Link

J. Assocn. Off. Agric. Chem., **44** (1961) 43–53
Chem. Abs., **55** (17 Apr 1961) 7687

Simple procedures are given for salting out the dye with NH_4 sulphate, retaining it on a cellulose chromatographic column, and determining the intermediate in an NH_4 sulphate eluate from the ultraviolet absorption (220–400 mμ) for FD&C Red No. 1, 2, 3 and 4 (C.I. Food Red 6, 9, 14 and 1), FD&C Blue No. 1 and 2 (C.I. Food Blue 2 and 1), FD&C Yellow No. 5 and 6 (C.I. Food Yellow 4 and 3), and FD&C Violet No. 1 (C.I. Food Violet 2). Usually only one intermediate is present in each dye. C.O.C.

Paper Chromatography of Permitted Food Dyes. I—C.I. Food Yellow 3

O. A. Valenciano and A. Ibara

Rev. asoc. bioquím. arg., **24** (121–2) (1959) 20–26
Chem. Abs., **55** (20 Mar 1961) 5793

Study of the paper-chromatographic migration of di-Na 1-(*p*-sulphophenylazo)-2-naphthol-6-sulphonate in graded 0–100% aq. soln. of methanol, ethanol, propanol, isopropanol, butanol, isobutanol, and pentanol on Whatman No. 1 filter paper. C.O.C.

Subsidiary Dyes in FD&C Colours (6-Sulpho-2-naphthylazo-2-naphthol and 8-Sulpho-2-naphthalazo-2-naphthol in FD&C Red No. 10-13)

L. Koch *J. Assocn. Off. Agric. Chem.*, **44** (1961) 56–58
Chem. Abs., **55** (17 Apr 1961) 7687

Details are given of a modified method (based on collaborative study) for determining 2,6- and 2,8-isomers in Lithol Red (1-sulpho-2-naphthylazo-2-naphthol, C.I. 15630). C.O.C.

Studies on Coal Tar Colours. XXVI—FD&C Red No. 2 (C.I. 16185)

W. B. Link *J. Assocn. Off. Agric. Chem.*, **44** (1961) 53–56
Chem. Abs., **55** (17 Apr 1961) 7687

A proposed method for preparing pure C.I. 16185 so that it is suitable as an analytical standard. The dye can be determined spectrophotometrically in absence of other coloured substances. Methods are given for detection of 6 subsidiary colours in C.I. 16185. C.O.C.

Quantitative Estimation of Azo Dyes by Direct Reductometric Titration with Vanadium (II) Sulphate

M. Matrka and Z. Ságner

Chem. prûmysl, **10** (1960) 474–475
Chem. Abs., **55** (3 Apr 1961) 6869

A solution of 0·06732 g Methyl Red (C.I. Acid Red 2) and 10 g NaK tartrate was titrated at 90°C with 0·1-N VSO_4 until the solution was colourless. This accounted for 54·5% of the dye. However, 97·4% could be accounted for by potentiometric titration using a polished Pt electrode *vs* satd. calomel electrode. In both cases the results were compared with the 100% yielded by titration with 0·1-N $TiCl_3$. 0·00025-M Methyl Red was added dropwise at 90°C to a mixture of 10 ml 0·1-N VSO_4 with 10 ml 0·1-N $FeNH_4(SO_4)_2$ and with 10 g NaK tartrate in 100 ml of water; immediate discoloration occurred and consumption of dye corresponded to the equivalent of V^{3+} salt formed. Analogous results were obtained with Methyl Orange (C.I. Acid Orange 52) and dyes of the type o-aminobenzoic acid → NW acid. C.O.C.

Paper Partition Chromatography of Alkyl-substituted 1-Phenylazo-2-naphthols

R. B. Smyth and G. G. McKeown

J. Chromatography, **5** (May 1961) 395–407

A number of alkyl-substituted 1-phenylazo-2-naphthols were prepared by the diazotisation and coupling of the following amines to 2-naphthol— aniline, *o*-, *m*- and *p*-toluidine, 2-ethyl, 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-dimethylaniline, and 2,4,5- and 2,4,6-trimethylaniline. The 3,5-dimethyl deriv. is reported for the first time. R_f values, determined by reversed-phase chromatography using mineral-oil-impregnated paper and acetone–water mixtures as developing solvents, are given. R_m values were calculated and are discussed in the light of chemical structure and chromatographic behaviour. F.J.

Chromatographic Analysis of Naphtol AS Compounds

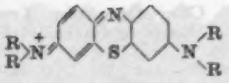
F. Pagani *Tinctoria*, **58** (Mar 1961) 107–108

15 Derivatives of 3-hydroxy-2-naphthoic acid and the corresponding commercial products of the Naphtol AS series were submitted to ascending paper chromatography. The R_f values were determined, and diethyl sulphamido-o-anisidine was used for identification. W.M.

R_f-Values of Some Thiazine Dyes

J. Chromatography, **5** (Apr 1961) D20

Tabulated R_f values of 22 thiazine dyes based on the structure



where R = H, CH_3, C_2H_5, C_3H_7 or mixed alkyl groups, are reported from K. B. Taylor, *J. Histochem. and Cytochem.*, 8, 248 (1960). Solvents used in this work were 2-N HCl and dioxan–2-N HCl (92·5 : 7·5). F.J.

Powder Chromatography for Estimating Carotene (C.I. Natural Yellow 26) in the Field

B. N. Majumdar and B. N. Gupta
Current Sci., (India), **29** (1960) 434–435
Chem. Abs., **55** (17 Apr 1961) 7143

The usual column chromatography for Carotene purification was compared with the use of powdered bonemeal shaken in a beaker with the petroleum ether extract containing the sample of Carotene. Xanthophylls and other non-carotenoid pigments were absorbed by the bonemeal in 30 min, the pure extract of Carotene was decanted, and assayed colorimetrically. This method does not separate the Carotene isomers but permits total assay. C.O.C.

Polarographic Estimation of Ti in Ferric Red (C.I. Pigment Red 101 and 102)

J. Stabryn *Chem. průmysl*, **10** (1960) 584–585
Chem. Abs., **55** (20 Mar 1961) 5983

The sample (2·5 g) was dissolved in conc. HCl, and $FeCl_3$ extracted from solution with ether. The aqueous layer was evaporated and the residue dissolved in water (50 ml). To some of this solution (20 ml), 6-M NH_4 acetate (15 ml) and 0·5% gelatin (1 ml) were added. The method of standard additions of Ti was used. Cathodic polarography was carried out from −0·6 to −1·9 v. The $E_{\frac{1}{4}}$ of Ti^{4+} is −1·12 v. Traces of Fe^{3+}, Cu^{2+}, Mn^{4+}, V^{5+} and Pb^{2+} have no effect on the estimation; NO_3^-, alkaline Cl^-, and SO_4^{2-} must not be present in the extracted sample. Extraction with ether must be done in darkness to prevent photochemical reduction of Fe^{3+}. C.O.C.

Organic Pigment Identification

M. Saltzman *Chem. Prod.*, **23** (1960) 563–565
Chem. Abs., **55** (17 Apr 1961) 7843

Describes a system for identifying organic pigments based on (*a*) the chemical classification of pigments by Vesce and Ryan (*Protective and Decorative Coatings*, Vol. II, 1942) and (*b*) use of spectrophotometric transmittance curves of solutions of pigments in many solvents. C.O.C.

A Method of Testing Dyeing Properties of Polyacrylonitrile Fibres

W. Pelz and D. Janneck
Faserforsch. und Textiltech., **12** (Mar 1961) 118–121

Staining with potassium permanganate solutions and microscopic examination of cross-sections of stained fibres are used to assess the dyeing properties of polyacrylonitrile fibres. W.R.M.

I.C.C.A. Standard 2:61— Alkali Solubility of Pulp

Svensk Papperstidning, **64** (30 Apr 1961) 291–293 (*in English*)
Norsk Skogindustri, **15** (Apr 1961) 151–153 (*in English*)

In this method, identical with SCAN 2:61, the pulp is treated with aq. NaOH (18 or 10%) at 20 ± 0·2°C for 60 min. Dissolved organic material is oxidised with potassium dichromate and conc. H_2SO_4, and excess of dichromate is titrated with freshly standardised ferrous ammonium sulphate, using ferroin as indicator. 11 References. R.A.

Rapid Moisture Determination in Leather

R. Stubbings and L. Ambrose
J. Amer. Leather Chem. Assocn., **56** (Apr 1961) 148–163

A comparison of dielectric constant and resistance as a measure of the moisture content of leather is made, to the advantage of the latter. Development of a D.C. resistance meter for measuring the moisture content of leather is described and the operating parameters are evaluated. A commercial instrument for the rapid, non-destructive measurement of moisture content over the range 9–40% is described; its application in tannery practice is indicated. J.W.D.

Correlation Between Wear Trials and Abrasion Tests on Sole Leather

R. G. Mitton
J. Soc. Leather Trades Chem., **45** (Apr 1961) 130–166

A description of experiments made in several countries to compare various types of abrasion machine as guides to the durability of sole leather. The choice of abrasive medium is important in view of the tendency of many types to become clogged with abraded particles. Independent wear trials on the same leathers in different countries correlate fairly well with one another, but the closeness of correlation depends upon the method of measuring the worn soles. Several machines give satisfactory results, apart from some difficulties with impregnated leathers, but further work is required in this direction. The type of abrading motion (reciprocating, planetary, etc.) and its speed do not appear to be important, nor does the size of the abrading surface, but pressure between abrasive and leather is important in certain machines. However, machines whose rates of abrasion differed by a factor of 100 or more gave equally good correlation with wear. Replicate tests are necessitated by variation from place to place on a bend of leather; several small samples give better results than one large one. Tests on a constant fraction of the total thickness of the leather gave a reasonable guide to the abrasive resistance of the whole thickness. Measurements of the energy required to abrade leathers give poorer correlation with durability in wear than do measurements of abrasion resistance, and are not recommended. J.W.D.

Quantitative Determination of Synthetic Resin in Finished Textiles

Textil-Rund., **16** (Mar 1961) 126–127

Method SNV 95 6 49 of the Swiss Standards Association P.B.S.

Determination of Urea- and Melamine-Formaldehyde Resin in Rayon Fabrics

F. Kočevar *Textil-Rund.*, **16** (Mar 1961) 109–114

The development of a more accurate method of determining synthetic resin is described. It is applicable to rayon having a crease-resistant finish and depends upon hydrolysis of the resin. A 1-g sample of washed material is boiled for 1 h with 50 ml lactic acid solution (200 ml lactic acid [density 1,21] and 10 g urea in 1 l. distilled water). This solution is poured off and the treatment repeated with fresh lactic acid solution. After being washed acid-free with hot and cold water, the sample is dried to constant weight. The loss of weight, after application of appropriate corrections, is the weight of resin. P.B.S.

Natural and Synthetic Rubbers

F. J. Linnig, M. Tryon, and E. J. Parks
Anal. Chem., **33** (Apr 1961) 127R–137R

A review of analytical methods for the two-year period ending October 1960. P.B.S.

Polymethine Dyes. VII— Polymethine Dyes Produced by Reaction of *p*-Dimethylaminocinnamaldehyde with Primary Aromatic Amines, Various Heterocyles, and Sulphonamides (Test for Sulphonamides) (IV p. 379)
Fastness of Dyed Textiles to Pleating Processes (X p. 394)

XV— MISCELLANEOUS

Model of Colour Vision

V. K. Lyapidevskiĭ *Doklady Akad. Nauk S.S.S.R.*, **134**, No. 2 (11 Sept 1960) 463–466

The functions of an animal eye are explained on the basis of a model containing two photocells (A and B) of different spectral characteristics. Irradiation produces the currents I_A and I_B which are recorded on an oscillograph as horizontal and vertical deviations respectively; $I_A + I_B$ signifies light intensity, I_A/I_B the colour. Thus, normal trichromatism is replaced by the view that neither cone nor rod vision is responsible for colour vision, the two differing merely in spectral characteristics. Anomalous colour vision and colour blindness are also dealt with. G.J.K.

Occupational Tumours of the Bladder
D. S. Poole-Wilson
Proc. Roy. Soc. Med., **53** (1960) 801–814
Chem. Abs., **55** (17 Apr 1961) 7702

Mainly a pathological review and interpretation with some new data. Differences in the activity of industrial organic compounds in producing bladder tumours are considered. There is no evidence that finished dyes are carcinogenic. Aniline is no longer regarded as causing bladder tumours, but some higher homologues of aniline are carcinogens. Because of its dangerous properties, 2-naphthylamine is no longer used in making dye intermediates in the U.K., Germany, and Switzerland. Because of potential dangers, *p*-aminobiphenyl has never been manufactured in the U.K. 53 References. C.O.C.

The Nature of Textile Evolution in the World
S. H. Scheuer
Canadian Textile J., **78** (17 Mar 1961) 27–31

The technical advances in the textile industry during the 1950s are reviewed and are described as revolutionary rather than evolutionary. Technical and commercial influences have combined to create a vast increase in consumption which will grow substantially in the 1960s owing to continued co-operative efforts in research and marketing. Improvements in machinery will be the central theme in the 1960s, but this must be matched by re-adjustment of commercial concepts, which should be viewed on an international basis. A new perspective and a more penetrating judgment in world affairs are mandatory. W.P.M.

Impressions of Teaching Institutions and Textile Works in the U.S.S.R.
C. Earland *J. Textile Inst.*, **52** (Mar 1961) P129–P134

A review, based on observations made during a lecture tour. The accommodation, staff and student members, and the courses offered at Moscow University, Mendelćef Institute of Chemistry, Moscow Textile Institute, and Leningrad Textile Institute are discussed. Mills were also visited. Safety and general working conditions in a Moscow weaving and finishing mill (built 1890) were very poor, but the light suitings produced by 95% female labour were of good quality. The mass production of clothing in a Leningrad factory was organised on a conveyor belt principle and each suit was handled by 180 girl operatives. The use of adhesives for bonding seams was being developed. The quality of the output was similar to that of British ready-made suits of intermediate price. The general impression was that there is little of value to be gained from Russian practice, but textile teaching methods are more practical in outlook than in the U.K. Teaching is concentrated in the Moscow and Leningrad Institutes which, with a total of 7000 students and an annual output of 1400 technologists, supply the whole country. E.C.

Intramolecular Charge-transfer Transitions from Olefinic Double Bonds to Carbonyl Groups
R. C. Cookson, R. R. Hill, and J. Hudec
Chem. and Ind., No. 18 (6 May 1961) 589–590

Compounds containing a carbonyl group and a double bond separated by one saturated carbon atom show, in certain cases, a new absorption band in the ultraviolet spectrum, which has been attributed to charge-transfer from the unsat. to the carbonyl group; it occurs only when the geometry is favourable for overlap of the orbitals concerned. Examples of cpd. are now reported where the interacting groups are separated even further. H.H.H.

Fluorescent Protein Tracing and the Fluorescent Antibody Method
R. C. Nairn *Endeavour*, **20** (Apr 1961) 78–84

Fluorescent dyes may be used to label proteins which are injected into animals and subsequently traced directly in histological sections by ultraviolet fluorescence microscopy. There are six photomicrographs in colour. J.W.D.

Viscosity Measurements in Process Control
P. H. Stirling and H. Ho
Ind. Eng. Chem., **53** (Apr 1961) 56A–59A

The use of viscosity measurements in process control is discussed in a general way. Then commercially available viscometers are classified according to operating principles and their value for various measurements is considered. P.B.S.

Group Screening Designs
W. S. Connor *Ind. Eng. Chem.*, **53** (Apr 1961) 63A–64A

The statistical design of experiments is considered for the case in which experimental error is appreciable and the concept of efficiency is complex. (See also J.S.D.C., **77** (June 1961) 276.) P.B.S.

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Apparatus for Shaking a Large Number of Flasks (XIV p. 397)
Applications of Complementary Tristimulus Colorimetry (XIV p. 397)

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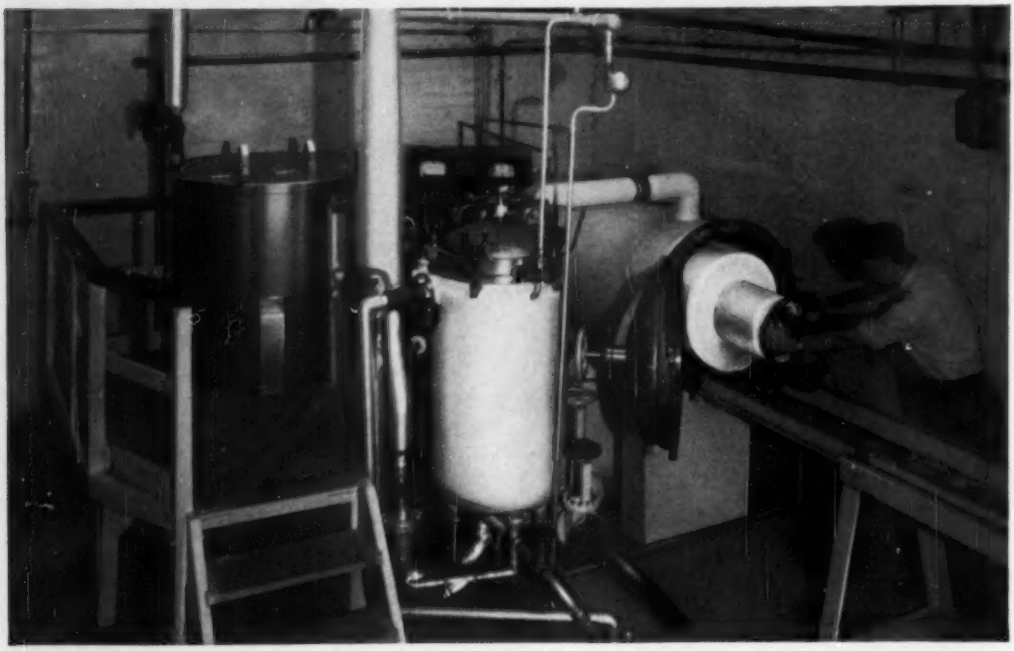

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THE MEASUREMENT OF COLOUR

A COURSE of five lectures, followed by five periods of practical work, will be given on Mondays at 7 p.m. from 9th October to 11th December 1961. Full details and forms of application may be obtained from the Head of the Department of Chemical Technology, Bradford Institute of Technology, Bradford 7.

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TEXTILE TECHNOLOGISTS

for the Technical Service section of the Yarn Sales Department. The company is erecting a large factory at Antrim, Northern Ireland, where nylon 6 continuous filament yarns will be manufactured for use in a wide range of textile processes

Applications are invited from established textile technologists in the age group 30–45 who are of A.T.I. standard or graduate equivalent. It is essential that they should have had several years practical experience in one or two branches of the textile industry, although this would not eliminate acknowledged experts in one field alone.

The fields to be covered by this group are all forms of knitting and associated problems of dyeing and finishing, winding, processing (doubling, bulking, brushing, etc.), weaving, together with associated problems in dyeing, printing and finishing of all types of woven fabrics. Included in the group will be a man (or men) with experience in the "making-up" trades.

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Symposium Dinner and Dance
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Demonstrations by the courtesy of CIBA CLAYTON LIMITED

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Application Forms together with details of Charges and Lectures and Social Functions have been circulated and further copies required are available from The General Secretary, The Society of Dyers and Colourists, Dean House, 19 Piccadilly, Bradford 1, Yorkshire (*Telephone* 25138)

PLEASE NOTE CLOSING DATE FOR APPLICATIONS IS MONDAY 4th SEPTEMBER

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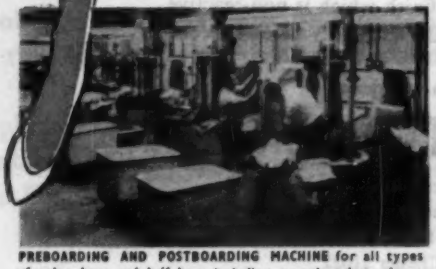

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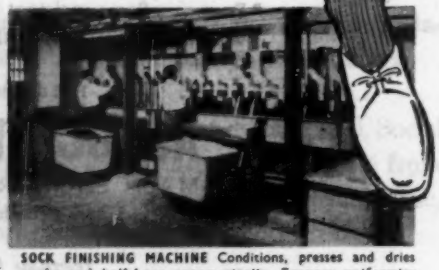

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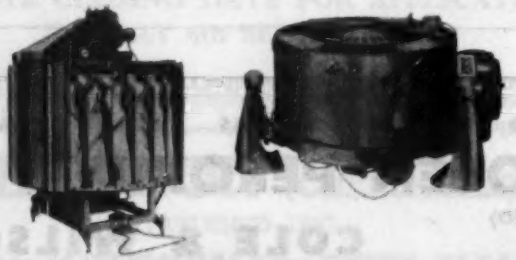

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Symposium at Zürich 11–14 October 1961

International Federation of Associations of Textile Chemists and Colourists (I.F.A.T.C.C.)

Congress at Noordwijk, Holland 25–27 April 1962

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